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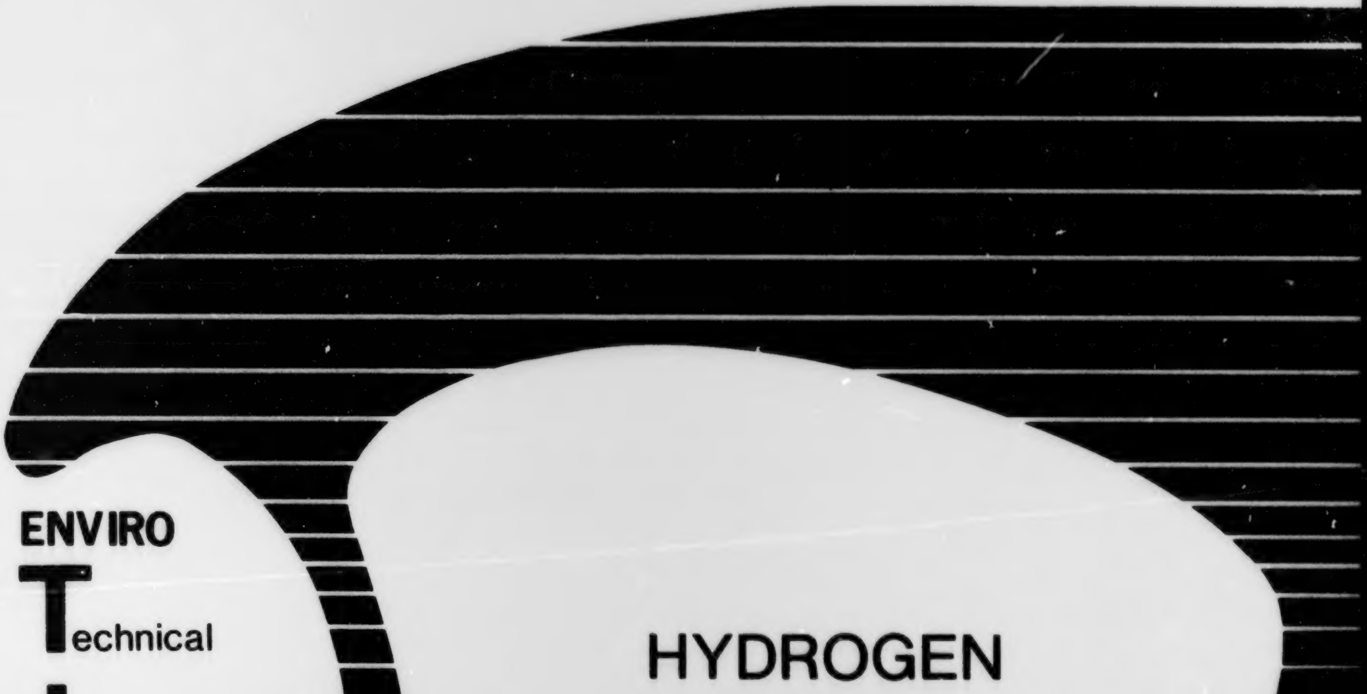

ENVIRO
Technical
Information for
Problem
Spills

HYDROGEN SULPHIDE

July 1984

Canada

85-1690/

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

HYDROGEN SULPHIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

July 1984

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

HYDROGEN SULPHIDE (H_2S)

Colourless gas with a rotten egg odour

SYNONYMS

Sulphur Hydride; Sulphuretted Hydrogen, Stink Damp, Acide Sulphhydrique (Fr.), Hydrogene Sulphure (Fr.)

IDENTIFICATION NUMBERS

UN No. 1053; CAS No. 7783-06-4; OHM-TADS No. 7216752; STCC No. 4905410

GRADES & PURITIES

Technical, 98.5 percent purity

C.P. Grade, 99.5 percent purity

IMMEDIATE CONCERNS

Fire: Flammable. Flashback may occur along vapour trail. Burns in air to produce sulphur dioxide

Human Health: Highly toxic by inhalation and contact. May fatigue the sense of smell and thus not provide warning of higher or continuing concentrations

Environment: Harmful to aquatic life in very low concentrations; threshold concentration for fresh- or saltwater fish is 0.5 ppm

PHYSICAL PROPERTY DATA

State: (15°C, 1 atm): gas
Boiling Point: -60.7°C
Melting Point: -85.5°C
Flammability: flammable
Vapour Pressure: 2026 kPa (25.5°C)
Density: 0.86 g/mL (liquid at -61°C)

Solubility (in water): 437 mL/100 mL (0°C); 186 mL/100 mL (40°C)
Behaviour (in water): floats; dissolves rapidly (boils)
Behaviour (in air): vapour is heavier than air
Odour Threshold: 0.0001 to 0.001

ENVIRONMENTAL CONCERNS

Toxic to aquatic and animal life in very low concentrations. Threshold concentration for fresh- or saltwater fish is 0.5 ppm. Injury to plants if exposed to >5 ppm in air over 24 hours. Hydrogen sulphide does not have bioaccumulation or food chain contamination potential.

HUMAN HEALTH

TLV®: 10 ppm (14 mg/m^3)
IDLH: 300 ppm

Exposure Effects

Inhalation: Poisonous if inhaled. Sense of smell may be fatigued and fail to give warning in high concentrations or after long exposure. Causes irritation of nose, throat and eyes, sneezing, headache, dizziness, nausea and vomiting, cold sweat, muscular weakness, unconsciousness and death

Contact: Skin contact causes irritation and painful inflammation. Eye contact causes irritation, watering and inflammation

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warnings: "FLAMMABLE" and "POISON". Keep noninvolved personnel away from spill site. Call fire department and notify manufacturer. Eliminate all sources of ignition including traffic and equipment. It is not advisable for inexperienced personnel to control the leak. Avoid skin contact and inhalation; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Flammable. Use foam, dry chemical, water spray, fog or carbon dioxide to extinguish. Do not extinguish fire unless release can be stopped. Cool fire-exposed containers with water. Stay clear of tank ends.

COUNTERMEASURES

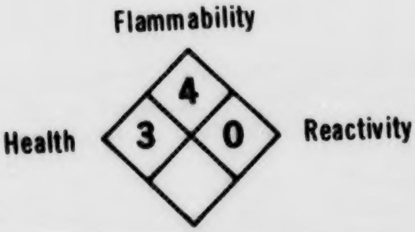
Emergency Control Procedures in/on

Soil: If spilled in liquid form, contain with mechanical or chemical barriers. Liquid will rapidly boil and convert to vapour

Water: Contain contaminated water by damming or water diversion. Use carbon absorption to remove

Air: Use water spray or fog to control and disperse flammable vapour. Control runoff for later treatment and/or disposal

NAS HAZARD RATING



NFPA
HAZARD
CLASSIFICATION

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas (Thio-Pet UM 1979) or colourless liquid (Bailar 1973)
Usual shipping state	Shipped as a liquified gas under its vapour pressure (HCG 1981)
Physical state at 15°C, 1 atm	Gas
Melting point	-85.5°C (CRC 1980)
Boiling point	-60.7°C (CRC 1980)
Vapour pressure	2026 kPa (25°) (CRC 1982) 1033 kPa (0°C) (Kirk-Othmer 1983)

Densities

Density	0.86 g/mL (liquid at -61°C) (CRC 1982) 0.99 g/mL (liquid at -60.7°C) (Kirk-Othmer 1983) 1.539 g/L (gas at 0°C) (CRC 1982)
Vapour density	1.189 (15°C) (air = 1) (Thio-Pet UM 1979)

Fire Properties

Flammability	Flammable gas (NFPA 1978)
Autoignition temperature	260°C (NFPA 1978)
Burning rate (liquid)	2.3 mm/min (CHRIS 1978)
Upper flammability limit	46.0 percent (v/v) (Matheson 1981; Kirk-Othmer 1983) 44.0 percent (v/v) (NFPA 1978)
Lower flammability limit	4.3 percent (v/v) (Matheson 1981; Kirk-Othmer 1983) 4.0 percent (v/v) (NFPA 1978)
Burning characteristics	Burns with a pale blue flame in air (Merck 1976)
Heat of combustion	661 kJ/mole (HCG 1981; Kirk-Othmer 1983)
Combustion products	Water and sulphur dioxide (HCG 1981)
Flashback potential	May travel considerable distance to a source of ignition and flash back (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge (MCA 1968)

Other Properties

Molecular weight	34.08 (CRC 1980)

Constituent components of typical commercial grade	>98 percent H_2S (HCG 1981)
Refractive index	1.374 (liquid) (CRC 1980) 1.0006 (gas at 25°C) (Matheson 1981)
Viscosity	0.0124 mPa•s (17°C) (CRC 1980)
Latent heat of fusion	2.38 kJ/mole (at melting point) (HCG 1981; Matheson 1981)
Latent heat of sublimation	20.42 kJ/mole (25°C) (JANAF 1971)
Latent heat of vaporization	18.7 kJ/mole (at boiling point) (HCG 1981)
Heat of formation	-19.96 kJ/mole (25°C) (Perry 1973) -20.64 kJ/mole (25°C) (CRC 1982)
Ionization potential	10.47 eV (Rosenstock 1977)
Heat capacity	
constant pressure (C_p)	1.004 kJ/(kg•°C) (25°C) (Matheson 1981) 1.06 kJ/(kg•°C) (HCG 1981)
constant volume (C_v)	0.80 kJ/(kg•°C) (HCG 1981) 0.757 kJ/(kg•°C) (25°C) (Matheson 1981)
specific heat ratio (γ) (C_p/C_v)	1.33 (Matheson 1981)
Critical pressure	9010 kPa (HCG 1981; Matheson 1981)
Critical temperature	100.4°C (HCG 1981; Matheson 1981)
Thermal conductivity	1.40 x 10^{-2} W/(m•K) (16°C) (CRC 1982)
Diffusivity	1.61 x 10^{-5} cm^2/s (in water at 25°) (Perry 1973)
pH of aqueous solution	4.1 (0.1 N solution 25°C) (CRC 1982)
Dipole moment	1.10 D (Matheson 1981)
Dielectric constant	1.004 (gas 0°C) (Matheson 1981) 9.05 (liquid at -78.5°C) (Matheson 1981)

Solubility

In water	437 mL/100 mL (0°C) (CRC 1982) 186 mL/100 mL (40°C) (CRC 1982)
In other common materials	Soluble in ethanol and carbon disulphide (CRC 1982) Very soluble in alkanolamines, soluble in methanol, acetone, propylene carbonate, sulfolane, tributyl phosphate, various glycols and glycol ethers. Also in n-methylpyrolidinone, 49 mL/g (20°C); hexane, 8.9 mL/g (20°C); and benzene, 16.6 mL/g (20°C) (Kirk-Othmer 1983)

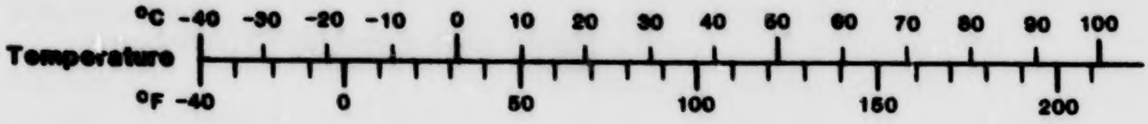
Vapour Weight to Volume Conversion factor

1 ppm = 1.413 mg/m^3 (20°C) (Verschueren 1977)

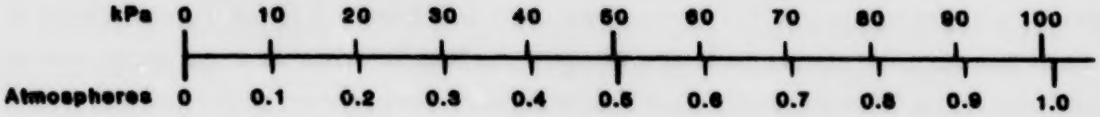
Structure

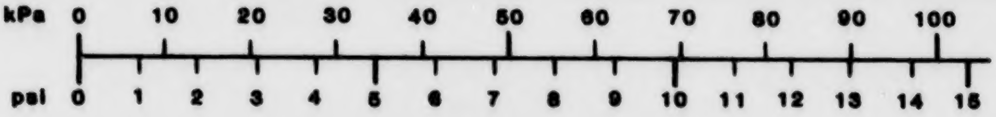
Hydrogen sulphide is the only thermodynamically stable binary sulphur-hydrogen compound that occurs frequently in nature. It is the sulphur analog to water. Due to the relative lack of hydrogen bonding, it exists as a gas under normal conditions. It is, however, easily liquefied by reduced temperature or increased pressure. The liquid is colourless, with about one-hundreth the viscosity of water.

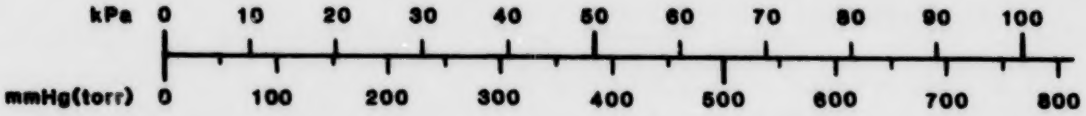
CONVERSION NOMOGRAMS


°C -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100
Temperature
°F -40 0 50 100 150 200

Pressure 1 kPa = 1,000 Pa


kPa 0 10 20 30 40 50 60 70 80 90 100
Atmospheres 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0


kPa 0 10 20 30 40 50 60 70 80 90 100
psi 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15


kPa 0 10 20 30 40 50 60 70 80 90 100
mmHg(torr) 0 100 200 300 400 500 600 700 800

Viscosity

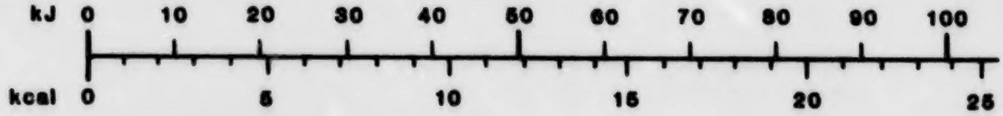
Dynamic 1 Pa·s = 1,000 centipoise (cP)

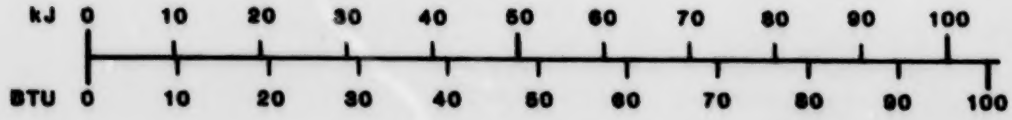
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1,000 J


kJ 0 10 20 30 40 50 60 70 80 90 100
kcal 0 5 10 15 20 25


kJ 0 10 20 30 40 50 60 70 80 90 100
BTU 0 10 20 30 40 50 60 70 80 90 100

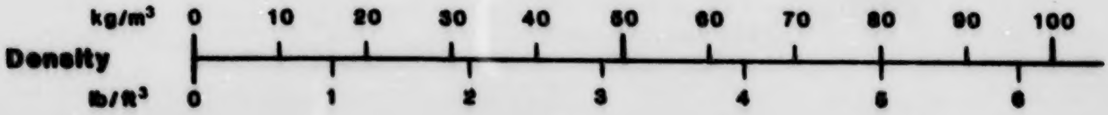

kg/m³ 0 10 20 30 40 50 60 70 80 90 100
Density
lb/ft³ 0 1 2 3 4 5 6

FIGURE 1

HYDOGEN SULPHIDE

VAPOUR PRESSURE vs TEMPERATURE

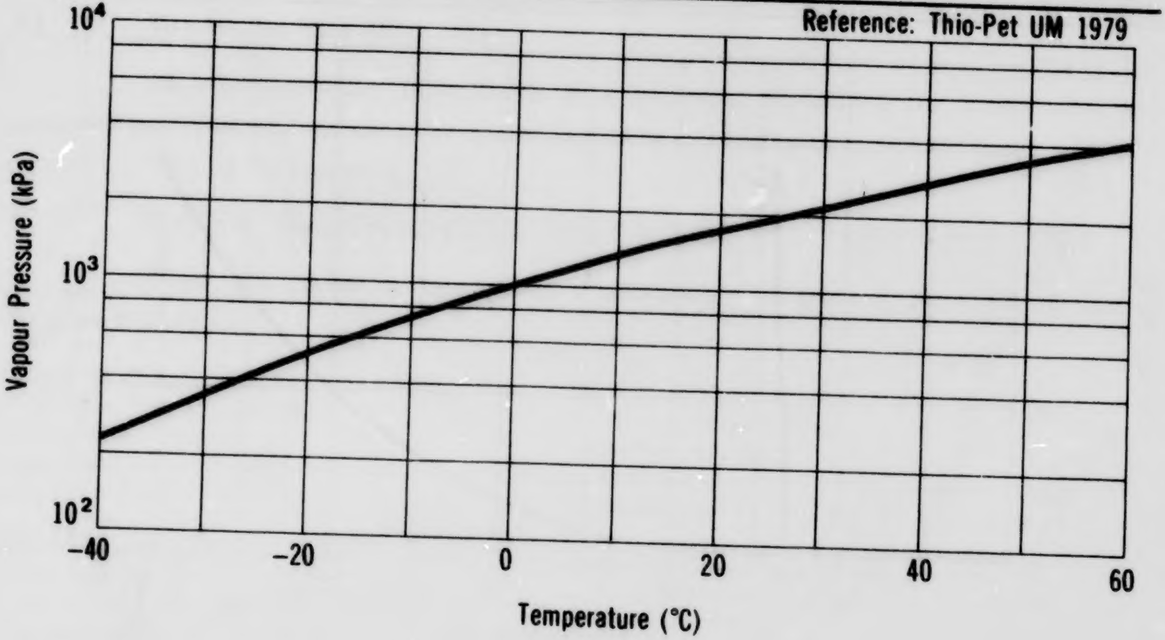

Reference: Thio-Pet UM 1979

FIGURE 2

HYDROGEN SULPHIDE

LIQUID DENSITY vs TEMPERATURE

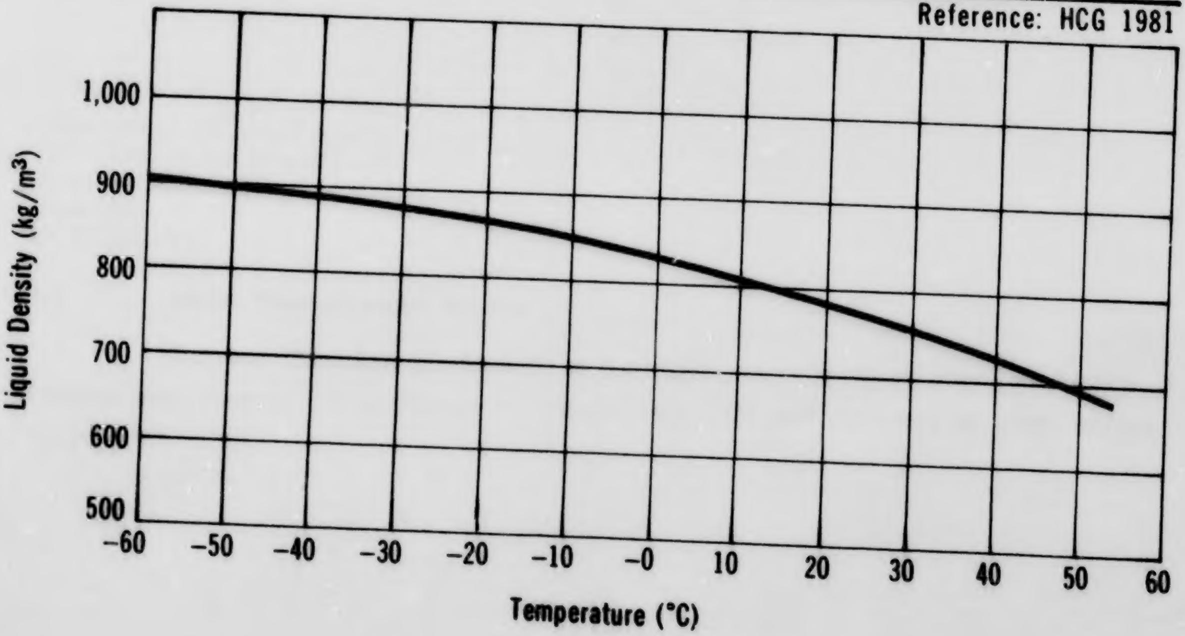
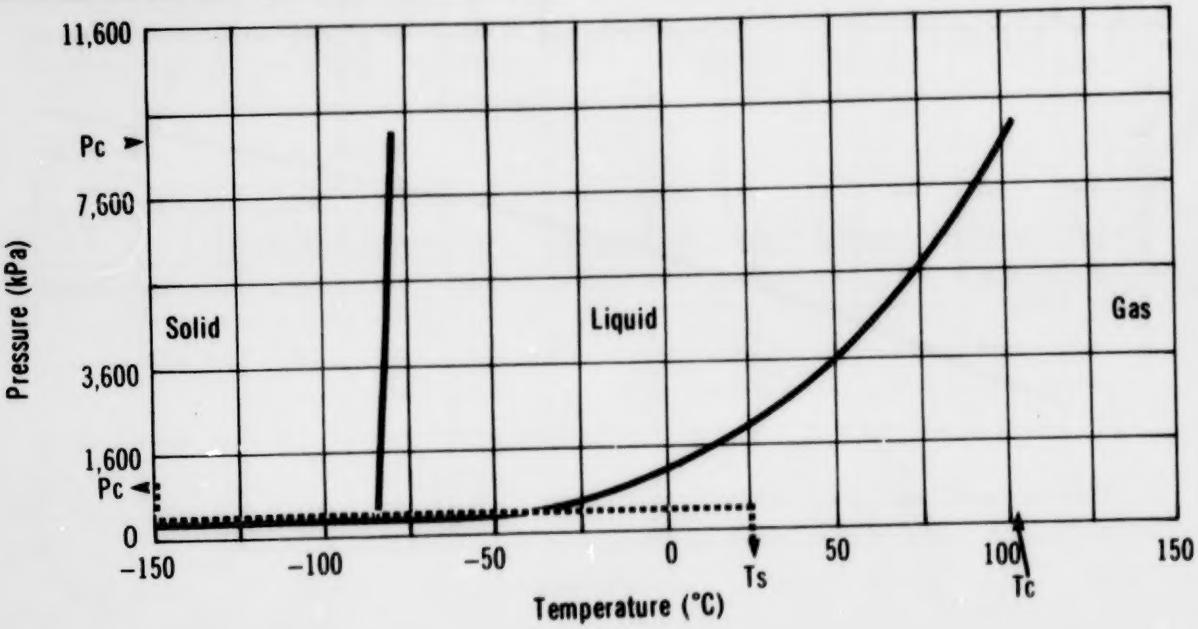

Reference: HCG 1981

FIGURE 3

HYDROGEN SULPHIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (HCG 1981)

Hydrogen sulphide is available in a technical or commercial grade with a minimum purity of 98.5 percent. It is also available in a high purity or C.P. grade with a minimum purity of 99.5 percent.

3.2 Domestic Manufacturers (CCR 1978; CBG 1980; Scott 1979)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Cornwall Chemicals Ltd.
P.O. Box 200, Station A
Willowdale, Ontario
M5N 5S8
(416) 226-7650

Sulconam Inc.
11450 Cherrier Street
Montreal, Quebec
H1B 1A6
(514) 645-1636

Sherritt Gordon Mines
P.O. Box 28
Commerce Court West
Toronto, Ontario
(416) 363-9241

Thio-Pet Chemicals Ltd.
1313 Edmonton Centre
Edmonton, Alberta
T5J 2Z1
(403) 426-1093

3.3 Other Suppliers (CBG 1980)

Air Products
2090 Steeles Avenue
Brampton, Ontario
L6T 1A7
(416) 791-2530

Canadian Liquid Air Co. Ltd.
1155 Sherbrooke Street West
Montreal, Quebec
H3A 1H8
(514) 842-5431

Matheson of Canada Ltd.
P.O. Box 89
Whitby, Ontario
L1N 5R9
(416) 668-3397

3.4 Major Transportation Routes

Current Canadian production of hydrogen sulphide takes place in Alberta, Ontario and Quebec. It is shipped in railway tank cars and cylinders to areas across Canada.

3.5 **Production Levels** (CCR 1978; CBG 1980; Thio-Pet UM 1979)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1980)
Cornwall Chemicals (C.I.L.), Cornwall, Ont.*	
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	4.5**
Sulconam, Montreal East, Que.	3.8***
Thio-Pet Chemicals, Ft. Saskatchewan, (1979) Alta.	3.6
TOTAL	11.9

* Captive use only
** Includes captive use (1/3)
*** Imported for sale

3.6 **Manufacture of Hydrogen Sulphide** (CCP 1978)

3.6.1 **Raw Materials.** Canada derives considerable amounts of hydrogen sulphide from "sour" natural gas and lesser amounts from other crude petroleum. Sour natural gas contains dissolved hydrogen sulphide, usually in the range of 1 to 20 percent, but sometimes up to 91 percent. The hydrogen sulphide is extracted by processing plants located primarily in Western Canada (CMI 1980).

3.6.2 **Process Description.** Hydrogen sulphide is an undesirable contaminant in natural gas and must be removed before the latter is used. This is accomplished by passing the sour gas upward through an absorption tower, countercurrent to an aqueous solution of either diethylamine, monoethanolamine, hot potassium carbonate, or sulfinol (mixture of alkanolamines, sulfolane and water). The resulting solution is then heated in a stripper tower where hydrogen sulphide gas is evolved. The dissolution of the hydrogen sulphide gas in these solutions results in the formation of a salt which will generally dissociate to the original materials upon heating. The extraction solution is then ready to be used again (CMI 1980; Kirk-Othmer 1983).

3.7 **Major Uses in Canada** (HCG 1981)

Hydrogen sulphide is used commercially in the manufacture of heavy water, to purify hydrochloric and sulphuric acids, to precipitate sulphides of metals, and to manufacture elemental sulphur, mercaptans, ethylene, nylon, soda ash, sodium hydrosulphide, and other materials. It is used as a reducing agent in cresylic acid recovery and as a reagent in analytical chemistry.

3.8 **Major Buyers in Canada** (Corpus 1983; CBG 1980; Percy 1983)

Ontario Hydro (Bruce Nuclear Power Development), Toronto, Ontario.
Air Products, Brampton, Ontario.
Matheson of Canada Ltd., Brampton, Ontario.
Atomic Energy Canada Ltd., Port Hawkesbury, Glace Bay, Nova Scotia.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Liquid hydrogen sulphide is usually transported as a liquefied gas under its own vapour pressure in steel cylinders and railway tank cars. All containers are equipped with safety devices and pressure tested at regular intervals. Ton containers (sometimes made from aluminum) may also be used in conjunction with multi-unit tank cars.

4.1.2 Cylinder. Hydrogen sulphide cylinders are constructed of seamless or forge-welded steel, with a net mass of 1.8 kg (4 lb.) to 91 kg (200 lb.). Cylinders must comply with CTC/DOT specifications 3A480, 3A2015, 3AA2015, 3AA480, 3B480, 3E1800, 4A480, 4BA300, 4B480, 4BA480 and 3E1800. Standard cylinder pressure is listed as 1737 kPa (252 psi) at 21°C. The 3A and 3AA cylinders, the low-pressure variety, are shorter and have a larger diameter. Classification is applied to both high- and low-pressure cylinders. Some of the specifications are shown in Table 2 and Figure 4 (Matheson 1981; Linde 1981).

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3A480	Seamless steel cylinder. Maximum service pressure 3312 kPa (480 psi).
3AA480	Seamless steel cylinder. Maximum service pressure 3312 kPa (480 psi). Steels definitely prescribed. Maximum carbon content 0.28 percent.
3B480	Seamless nickel cylinder. Maximum service pressure 3312 kPa (480 psi).
4A480	Forge-welded steel cylinder. Maximum service pressure 3312 kPa (480 psi).
4B480	Welded and brazed steel cylinder. Maximum service pressure 3312 kPa (480 psi).

TABLE 2 CYLINDER SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
4BA480	Welded and brazed steel cylinder. Made of definitely prescribed steels. Maximum service pressure 3312 kPa (480 psi).
3E1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Maximum diameter: 51 mm (2 in.). Maximum length: 610 mm (24 in.).

* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.3 Railway Tank Cars. Railway tank cars designated for the transport of hydrogen sulphide are constructed of steel and have a nominal capacity of 68 000 L (15 000 Imp. gal.). The cars comply to CTC/DOT specifications 105A600W and 120A600W. The former is the most commonly used for this service and is described in Table 3 and depicted in Figure 5. Specifications for this tank car are given in Table 4. There is also a special railway car, CTC/DOT specification 106A800X, for transporting multiple ton containers of hydrogen sulphide. The car is described in Table 3 (TCM 1979; RTDCR 1974).

Tank cars are equipped with 102-254 mm (4-10 in.) of foam or cork protected by a steel jacket. The only opening permitted in the tank is a single manway located in the centre at the top. Five valves are mounted inside the dome cover. Four of these are ball valves; the fifth, mounted in the centre, is a safety relief valve (TCM 1979). Two ball valves are for unloading liquid hydrogen sulphide and two are connected to the vapour space (MCA 1968). Under each discharge outlet is an eduction pipe fastened to the manway cover and extending to the bottom of the tank. The safety relief valve is of the spring-loaded type and is usually combined with a breaking pin assembly. A 19 mm (3/4 in.) thermometer well may also be provided on top of the car (TCM 1979).

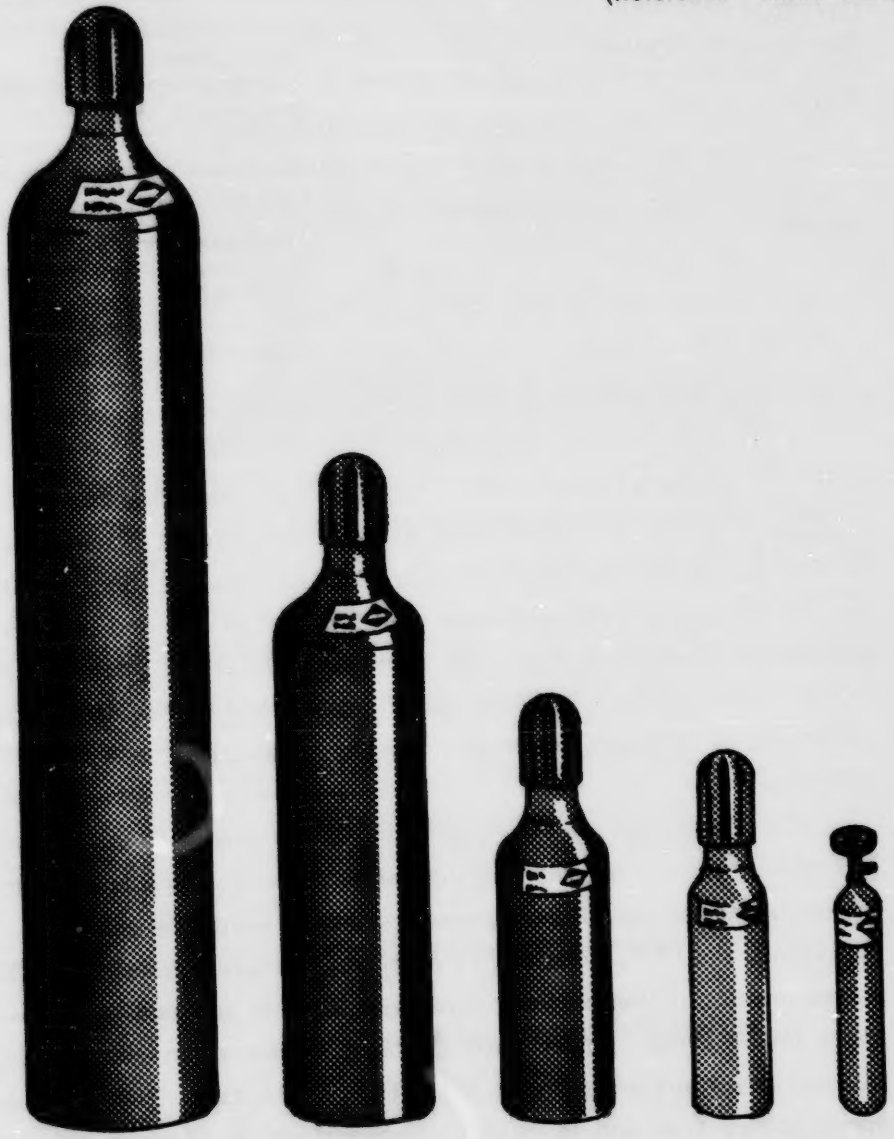
4.2 Off-loading

4.2.1 Off-loading Storage Equipment and Procedures for Cylinders. The following points should be observed when handling and storing containers (HSUM 1979):

FIGURE 4

COMMON GAS CYLINDERS

(Reference - LINDE 1981)



Industry designation		**K**	**Q**	**G**	**F**	**LB**
Approx. size	**(mm)**	229×1320	178×787	152×508	102×432	51×330
	(in)	9×52	7×31	6×20	4×17	2×13
Approx. weight (empty)	**(kg)**	60	29	13	5	1
	(lb)	132	65	29	10	4

TABLE 3 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A600W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Safety valve (3100 kPa) (450 psi). Bottom outlet or washout prohibited.
106A800X	Multiple unit with removable steel uninsulated tanks mounted on underframe. Tanks have fusion-welded longitudinal tank seam and forge-welded head seams. Popular name is "Ton Container". Tanks equipped with loading and discharge valves and safety vent set for pressure not exceeding 4140 kPa (600 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

- Valve protection hoods should be in place.
- Containers should not be stored near ventilator systems.
- Store to minimize external corrosion.
- Store cylinders upright.
- Store full and empty containers separately.
- Do not store reserve cylinders with those containing oxygen or highly oxidizing materials.

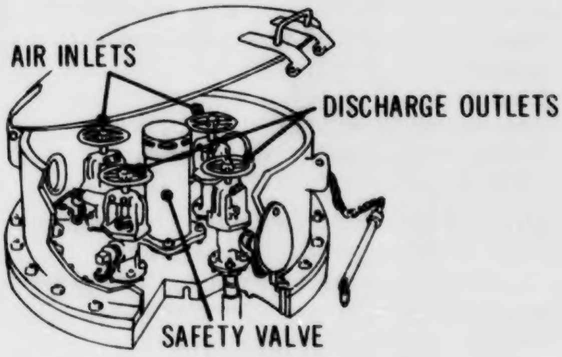
Cylinders deliver hydrogen sulphide gas when in an upright position and liquid when in an inverted position. It is advisable to use a flexible hose connection between the cylinder regulator and the permanent piping/receiving system to prevent unnecessary vibration and to facilitate the connect/disconnect procedure. A check valve or trap should be used to prevent suckback into the cylinder. All equipment and lines used with hydrogen sulphide should be grounded. Self-contained breathing apparatus should be readily available for use in an emergency. It is always good practice to use cylinder sizes which can be emptied in a reasonably short amount of time (Matheson 1981).

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars. The following precautionary steps must be taken (MCA 1968):

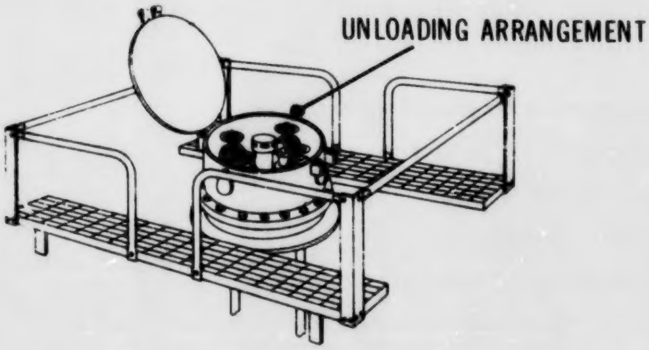
FIGURE 5

RAILWAY TANK CAR - CLASS 105A600W

Reference: TCM 1979, RTDCR 1974


AIR INLETS
DISCHARGE OUTLETS
SAFETY VALVE

Detail of top unloading arrangement


UNLOADING ARRANGEMENT

Detail of loading platform

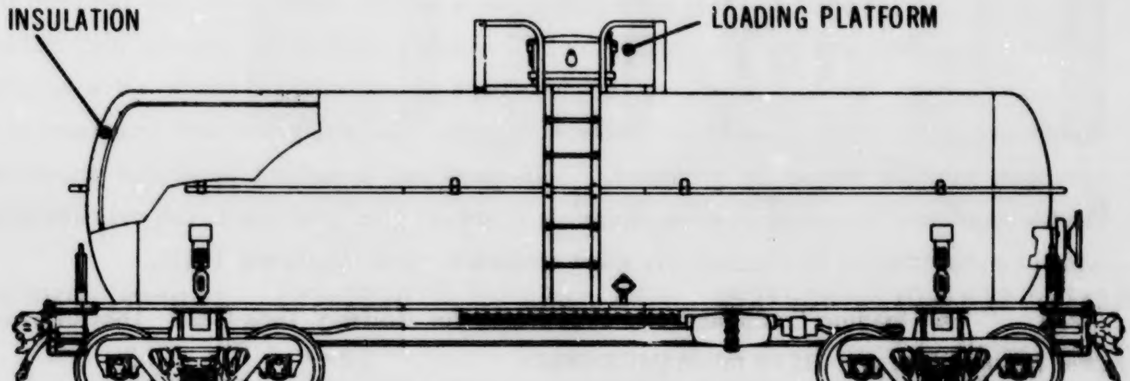

INSULATION
LOADING PLATFORM

Illustration of tank car layout

TABLE 4 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A600W (TCM 1979; RTDCR 1974)

Description			
Overall			
Nominal capacity	68 000	L	(15 000 gal.)
Car weight - empty	50 200	kg	(110 600 lb.)
Car weight - (max.)	119 000	kg	(263 000 lb.)
Tank			
Material	Steel		
Thickness	170-24	mm	(11/16 - 15/16 in.)
Inside diameter	2.6	m	(102 in.)
Test pressure	4 140	kPa	(600 psi)
Burst pressure	10,300	kPa	(1500 psi)
Approximate Dimensions			
Coupled length	17	m	(57 ft.)
Length over strikers	16	m	(55 ft.)
Length of truck centers	13	m	(44 ft.)
Height of top of grating	4	m	(12 ft.)
Overall height	5	m	(15 ft.)
Overall width	3.2	m	(127 in.)
Length of grating	2-3	m	(7-10 ft.)
Width of grating	1.5-2	m	(5-6 ft.)
Loading/Unloading Fixtures			
Unloading connection	25 mm (1 in.) via valve and 32 mm (1 1/4 in.) check valve		
Valving	2 unloading connections and 2 valves to vapour space		
Safety Devices	Safety relief valve set at 3 100 kPa (450 psi)		
Insulation	102-254 mm (4-10 in.) foam or cork insulation		

- Unloading operations to be performed only by properly instructed personnel.
- Dead-end siding used only for hydrogen sulphide rail cars to be provided.
- Brakes must be set, wheels chocked, proper derails employed, and appropriate placards displayed.
- Suitable operating platform to be provided at unloading point.

- Sparks from tools and static discharge must be avoided.
- Car must be grounded before loading or unloading arms are connected (HSUM 1979).
- Ensure that storage tanks are of sufficient volume to hold contents of tank car.

The railway tank car may be unloaded by vapour pressure or by pump. Chiksan or equal joints are recommended for unloading arms (HSUM 1979). When using the vapour pressure method, liquid is discharged from one of the two liquid valves and/or gas from one of the gas valves into the storage system. Liquid may also be pumped from one of the liquid valves into a storage tank.

4.2.3 Specifications and Materials for Off-loading Equipment. The components of a typical off-loading system handling hydrogen sulphide at commonly employed temperatures and pressures include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Generally, anhydrous hydrogen sulphide is of low corrosivity to carbon steel, aluminum, Inconel, Stellite, and 304 and 316 stainless steels. Hard steels, however, especially if stressed, are susceptible to hydrogen embrittlement by hydrogen sulphide. This may be avoided by using a Teflon coating, 316 stainless steel, or age-hardened Inconel. Sulphide stress cracking is most severe in the -7 to 49°C range. Severe sulphidation can occur at elevated temperatures; the resultant sulphide scale is of little protective value against further corrosion because metal sulphides have a low melting point and adhere poorly to metal surfaces. Nickel-base and high-nickel alloys, for example, generally have poor resistance to sulphides at high temperature, but are very resistant to sulphide attack under simulated deep oil-well and gas-well environments. Aluminum, however, has an excellent resistance and is considered a Class A material of construction for either wet or dry hydrogen sulphide. Wet hydrogen sulphide, on the other hand, is very corrosive to carbon steel, with corrosion rates being as high as 2.5 mm per year. High-strength steels may be susceptible to stress corrosion cracking. Steels satisfactory for use with wet hydrogen sulphide include 316 stainless containing 2.5 percent Cr and 1 percent Mo, 4-6 percent Cr and 0.5 percent Mo, 2-S or 3-S aluminum alloy, or 18-8 chrome-nickel stainless. All percents are by weight. 316 and 310 stainless steels can be used to handle hydrogen sulphide vapour to about 260°C and at higher temperatures, respectively. Wet hydrogen sulphide will corrode copper and brass; dry gas will only tarnish brass and not adversely affect its use (Matheson 1981; CE 1980, 1982; Kirk-Othmer 1983).

Pipes and fittings should be of Schedule 80 seamless black iron or carbon steel for dry hydrogen sulphide use (HSUM 1969). If strength properties are not a problem, aluminum or 316 stainless steel may be used (Matheson 1981).

Pipeline joints should preferably be flanged or welded (HSUM 1969). If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints.

Flexible connectors, consisting of natural rubber hosing or stainless steel piping with swivel joints, should be installed between containers and rigid piping systems. Gaskets may be Buna N. For valving, use cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride (DCRG 1978).

Pumps similar to the sealless centrifugal or positive displacement types are recommended. Liquid end or pump bowl must be 304 or 316 stainless steel, fully annealed. Wear rings and other wearing material should be Monel (HSUM 1979).

Storage tanks may be of steel construction, though stainless steel may be used to suit either dry or wet conditions at room temperature.

4.3 Compatibility with Materials of Construction

The compatibility of hydrogen sulphide with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

Recommended:	This material will perform satisfactorily in the given application.
Conditional:	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
Not Recommended:	Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Conditions		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	(1)	(2), dry	Black Iron (HSUM 1969; Matheson 1981)		
	(1)	(2), dry	Steel (3) (HSUM 1969; Matheson 1981)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Conditions		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
	(1)	(2)	NR (DCRG 1978)		
	(1)	(2)	SS (3) (DCRG 1978)		
	(1)	24, wet	Chlorinated Polyether (DCRG 1978)		
	(1)	60, dry	PVC I & II (DPPED 1967)		
	aq. sol'n (4)	60	PVC I & II (DPPED 1967)		
	(1)	66, dry, wet	PVDC (DCRG 1978)		
	aq. sol'n (4)	66	PVDC (DCRG 1978)		
	(1)	79, dry, wet	PP (DCRG 1978)		
	aq. sol'n (4)	79	PP (DCRG 1978)		
	(1)	107, dry	Chlorinated Polyether (DCRG 1978)		
	aq. sol'n (4)	107	Chlorinated Polyether (DCRG 1978)		
	aq. sol'n (4)	107	PVDF (DCRG 1978)		
	(1)	135, dry, wet	PVDF (DCRG 1978)		
	(1)	Op. lim., dry	PVC I, ABS, PE (MWPP 1978)		
	aq. sol'n (4)	Op. lim.	PVC I, ABS (MWPP 1978)		
	aq. sol'n (4)	(2)			PE (MWPP 1978)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Conditions		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Gaskets	(1)	(2)	NBR (DCRG 1978)		
3. Valves	(1)	(2), (6)	Chlorinated Polyether (5) (DCRG 1978)		
	(1)	(2), (6)	PVDC (5) (DCRG 1978; Kirk Othmer 1983)		
	(1)	(2), dry, wet	SS 316 (JSSV 1979)		
	(1)	(2), dry	Brass (Matheson 1981)		
4. Pumps	(1)	(2), dry (7)	SS 304 (HSUM 1979; Kirk-Othmer 1983)		
	(1)	(2), dry (6), wet (6)	SS 316 (HSUM 1979; Kirk-Othmer 1983)		
	aq. sol'n (4)	(2)	SS 304 (8), 316 (HIS 1969)		
5. Storage	(1)	RT, dry, wet	SS (3) (9)		
6. General (10)	(1)	(2), dry	SS, 304,316		
			Carbon Steel		Hard Steels (Kirk-Othmer 1983)
			Al, Inconel Stellite, TFE (11) (Kirk-Othmer 1983)		Nickel-based Alloys (12) High-nickel Alloys (12) (CE 1980)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Conditions		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
6. General (Cont'd)		(2), wet	Al, SS 316 (13, 14) 2-S Al Alloy 3-S Al Alloy SS 18-8 (Kirk-Othmer 1983)		Steel (15) Cu, Brass Carbon Steel (Kirk-Othmer 1983)
	(1)	20, dry	SS 302, 304 SS 316, 430 (ASS)		
	(1)	20, wet	SS 316 (ASS)	SS 302, 304 430 (ASS)	
	saturated	21, aq.	Ti (AMC; FMT)		
	saturated	Room Temp., aq.	Ta (AMC)		
	concentrated	23, aq.			Nylon (Zytel 101) (CIL 1964)
	100%	24, dry	Concrete, Wood (CDS 1967)		
	100%	24, wet		Wood (CDS 1967)	Concrete (CDS 1967)
	100%	24–100, dry, wet	Glass (CDS 1967)		
	saturated	40, aq.	uPVC, IIR, PE, EPDM, PP, CSM (GF)	NR, CR, NBR FMP (GF)	POM (GF)
	(1)	49, dry	PP (TPS 1978)		
	aq. sol'n (4)	49	PP (TPS 1978)		
	100%	60, dry	uPVC, IIR, PE, EPDM PP, FMP, NR, CSM, NBR (GF) PVC (TPS 1978)	POM (GF)	CR (GF)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Conditions		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
6. General (Cont'd)	aq. sol'n (4)	60	PVC (TPS 1978)		
	saturated	60, aq.	PE, EPDM, PP, CSM, IIR (GF)	uPVC, FPM, NR (GF)	POM, CR, NBR (GF)
	(1)	66, dry		PP (TPS 1978)	
	aq. sol'n (4)	66		PP (TPS 1978)	
	(1)	85, dry	CPVC (TPS 1978)		
	aq. sol'n (4)	85	CPVC (TPS 1978)		
	1	121, dry	PVDF (TPS 1978)		
	1	to 205 (16)	SS 316 (ASS) IIR, EPDM (GPP)	SS 302, 304 (ASS) CR (GPP)	NR, NBR SBR (GPP)
	1	<260, (16) vapour	SS 316 (Kirk-Othmer 1983)		
	1	>260, (16) vapour	SS 310 (Kirk-Othmer 1983)		
	1	>418 (16)	Alonized Steels (API)		

1. Assumed to be 100 percent
2. Not specified
3. Type not specified
4. Concentration not specified
5. Lining on cast iron or steel
6. Assumed wet or dry
7. Assumed dry
8. Validity questioned
9. No reference given
10. It is assumed materials specified under this condition may be used for other specific applications
11. Used as a coating
12. High temperature application
13. With 2.5 percent Cr and 1 percent Mo
14. With 4-6 percent Cr and 0.5 percent Mo
15. High strength
16. Dry or wet not specified

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
AL	Alonized steels (≥20% Al)
	Aluminum
	Brass
	Black Iron
	Carbon Steel
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
	Copper
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
	Inconel
IIR	Isobutylene/Isoprene Rubber (Butyl)
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
	Nylon (Zytel 101)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (followed by grade)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
	Steel
SBR	Styrene/Butadiene (GR-S, Buna S) Rubber

TABLE 6 MATERIALS OF CONSTRUCTION (Cont'd)

Abbreviation	Material of Construction
SS (followed by grade)	Stainless Steel
	SS 18-8 (Chrome-nickel stainless)
	Stellite
Ta	Tantalum
Ti	Titanium
TFE	Teflon
uPVC	Unplasticized Polyvinyl Chloride
	Wood

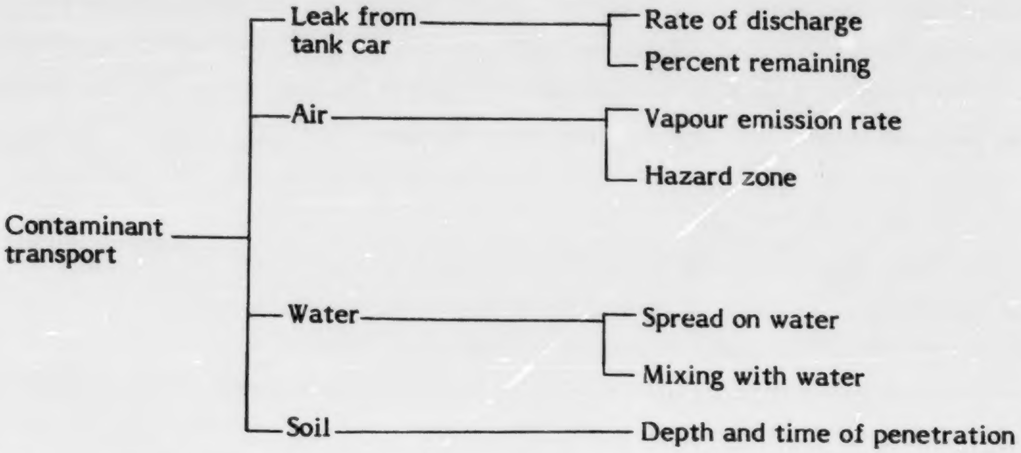
5 CONTAMINANT TRANSPORT

5.1 General Summary

Hydrogen sulphide is a known essential link in the natural sulphur cycle and is present in the atmosphere in the 3-30 $\mu g/m^3$ range. It is produced, for example, by anaerobic bacterial action in soil and marshes. In general, hydrogen sulphide is only an occasional and local pollutant. This man-made pollution can come from sources such as paper mills, handling accidents, gas-well blowouts, and transportation accidents. The former two sources may produce significant and harmful amounts of the gas; the latter two have the potential to release extremely large amounts of the toxic material. The gas evolving from a well blowout can contain in excess of 90 percent hydrogen sulphide. The amount which will be released to the atmosphere from a point source, at a relatively constant rate for an undetermined length of time, is generally much lower. Transportation accidents have the potential for a catastrophic release of up to 68 000 L per railroad tank car per accident. This latter mode will receive the major attention for the remainder of this section; it should be emphasized, however, that the plume models can also be applied to the constant point source release.

Hydrogen sulphide is transported as a liquefied gas in cylinders of various sizes and in railway tank cars. Release of hydrogen sulphide into the environment as the result of an accident can be primarily gaseous from a puncture in the upper portion of the tank car, or liquid from a puncture below the liquid level. If the leak is catastrophic, the released liquid will form a boiling pool that will spread on the surface of contact, whether water or ground. Since hydrogen sulphide is liquefied under pressure, the initial release will also be in the form of a vapour cloud. Concurrent with the spreading of the liquid will be rapid boiling, with some "popcorn" effect, and vapour formation due to the high volatility of the liquid.

When spilled on water, some of the material will dissolve during the boiling/vaporization process. The vapour cloud will tend to stay close to the water surface since its vapour density is greater than air. Spreading of this cloud will be a function of the weather conditions. The dissolved hydrogen sulphide will stay primarily in molecular form. Rate of diffusion will depend on the water conditions. When spilled on soil, however, vaporization will be the primary event, with adsorption onto the soil being secondary. The rate of adsorption will be dependent on soil type, its degree of saturation with water, plus other factors. Downward transport of the material, if it occurs at all, may cause environmental problems.



5.2 Leak Nomograms

5.2.1 Introduction. Hydrogen sulphide is commonly transported in railway tank cars as a liquid under pressure at ambient temperature. While the capacity of the most commonly used railway tank car is 68 000 L, one size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. The dimensions of this standard tank car are approximately 2.75 m in diameter and 13.4 m long, with an internal volume of about 80 000 L.

To facilitate nomogram preparation, certain assumptions regarding liquid discharge rate and vapour emission rate have been made. These assumptions are: 1) a puncture below the liquid level dictates that all liquid above the puncture will discharge; 2) during venting of gas from a puncture above the liquid level, the liquid will remain at a constant temperature; 3) all liquid will vaporize from a tank car with a puncture above the liquid level; and 4) the ambient liquid temperature is 40°C. Under "real world" conditions, other possibilities exist. It is conceivable that liquid discharging from a small puncture may form water ice around the puncture to the point of self-sealing. Isothermal conditions during gas venting will not be maintained as the liquid will cool during the vaporization process. Also, it is highly probable that during the venting of the gaseous hydrogen sulphide, water ice will form around the puncture and possibly on the surface of the liquid, starting at the liquid/metal interface. All of these possible conditions will tend to slow the release process and may ultimately lead to a self-sealing condition. The latter condition could possibly cause emergency personnel to believe the tank car is empty.

Finally, an assumed temperature of 40°C for the liquefied gas is quite high for Canada, even in summer.

If a tank car filled with liquefied hydrogen sulphide is punctured on the bottom, it can be assumed that all of the contents will drain from the car. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole area (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

If a tank car is punctured along the top or at any point above the liquid level, gas will be vented. For purposes of nomogram preparation, it can be assumed that gas will be vented until all of the liquid has vaporized and the internal and external pressures have equalized. It can also be assumed that the liquid will remain at a constant temperature equal to the ambient temperature (T). Under such assumptions, the vapour emission rate (Q) will remain constant during the vaporization of the entire liquid volume. The vapour emission rate is a function of the internal tank pressure, which is equal to the saturated vapour pressure of the liquid at temperature (T). For purposes of this exercise, the assumed ambient temperature for the internal contents of the tank car is 40°C, yielding a saturated vapour pressure of 2900 kPa (Figure 1). The assumption of isothermal conditions during the venting process will maximize the rate of gas release from the tank car and will probably represent a worst case situation for most emergencies involving a puncture above the liquid level.

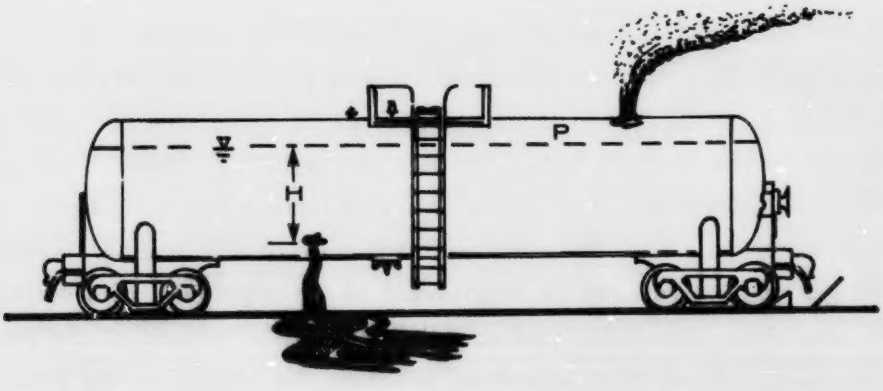


FIGURE 6 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The purpose of the nomograms is to provide a simplified means to obtain the time history of liquid discharge or gas venting processes. As mentioned previously, these processes are based on assumptions that imply "worst case" conditions. The details of the models used to calculate the discharge/venting rates are described in the Introduction Manual.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid discharge. The standard tank car (2.75 m ∅ x 1.34 m long) is assumed to be initially full (at t=0) with a volume of about 80 000 L of hydrogen sulphide at 40°C.

Figure 7: percent remaining versus time. Figure 7 provides a means of estimating the percent of hydrogen sulphide remaining in the standard tank car after the time of puncture, for a number of possible hole diameters. The hole diameter (d) is actually an equivalent diameter and can be applied to a noncircular puncture such as expected with a rip. The discharge rate will remain relatively constant as the tank car empties since isothermal conditions are assumed and thus the vapour pressure remains constant. The force due to vapour pressure will predominate over gravitational force.

Figure 8: Discharge rate versus equivalent diameter of puncture. Figure 8 provides a means of estimating the maximum discharge rate, q (L/s), for a number of equivalent hole diameters.

5.2.2.2 Top puncture - gas venting. The same standard tank car and basic assumptions used in Section 5.2.2.1 apply here.

Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of hydrogen sulphide remaining in the standard tank car after the time of puncture, for a number of possible hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture. As isothermal conditions have been assumed, the internal pressure and venting rate are constant. This results in a "worst case" estimate for vapour loss. The values presented here are independent of tank car size.

Figure 10: Discharge rate versus equivalent diameter of puncture. Figure 10 presents the relationship between discharge rate, q (kg/s), and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the

FIGURE 7

HYDROGEN SULPHIDE

PERCENT REMAINING vs TIME

Puncture in Bottom of Tank car

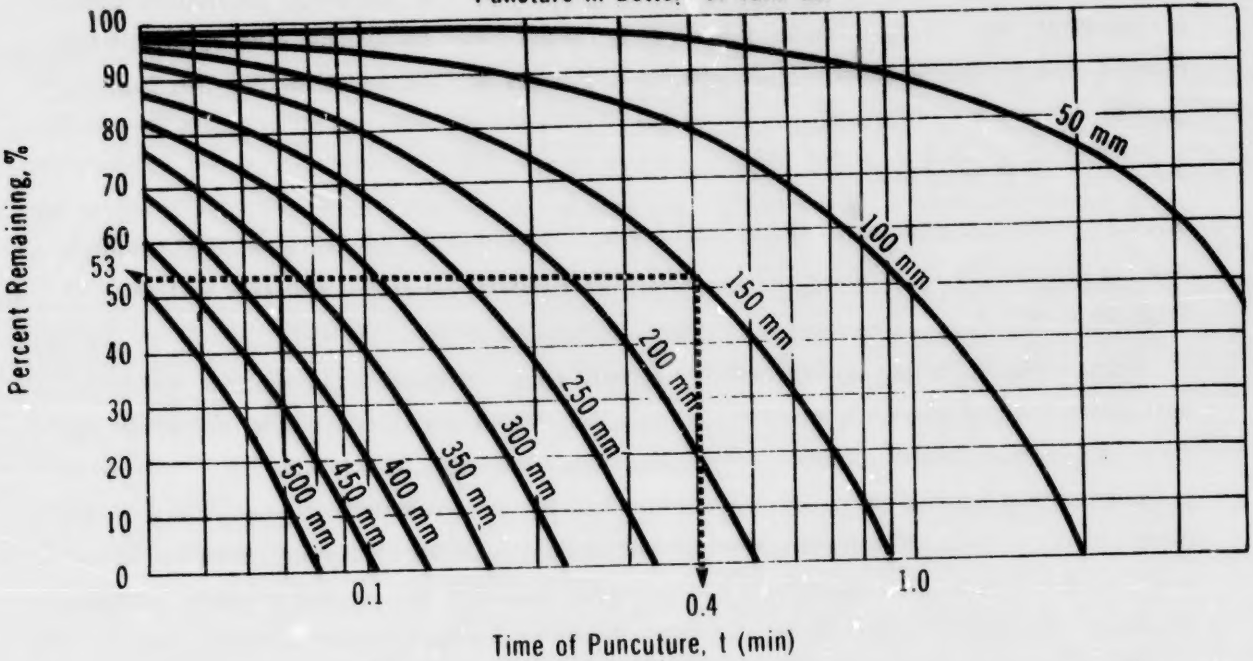


FIGURE 8

HYDROGEN SULPHIDE

DISCHARGE RATE vs PUNCTURE SIZE

Puncture in Bottom of Tank car

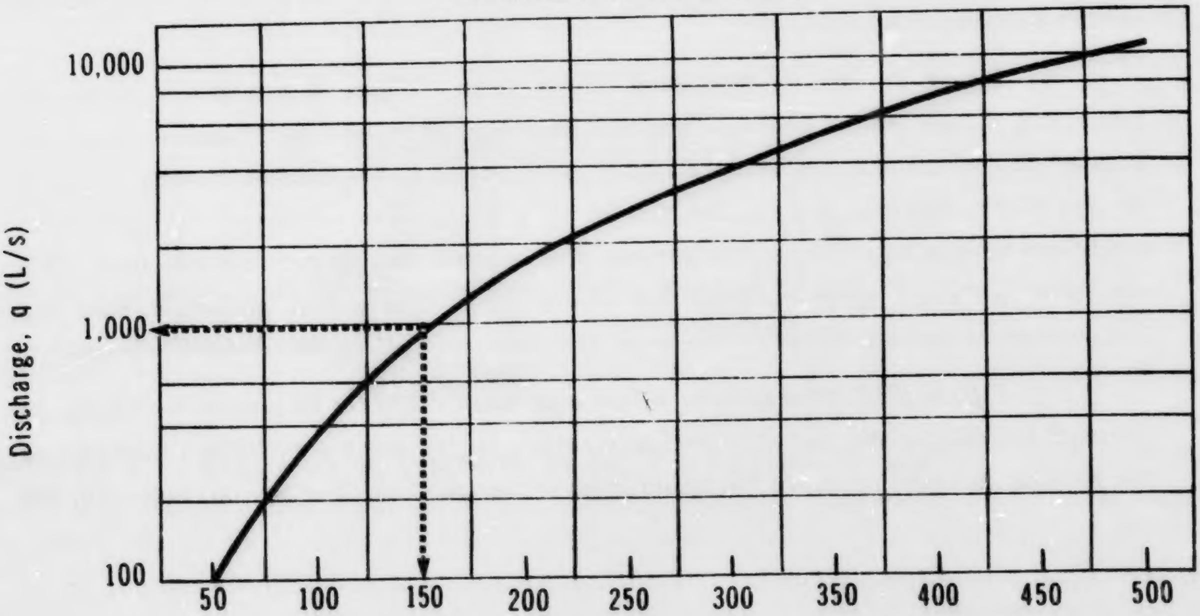


FIGURE 9

HYDROGEN SULPHIDE

PERCENT REMAINING vs TIME

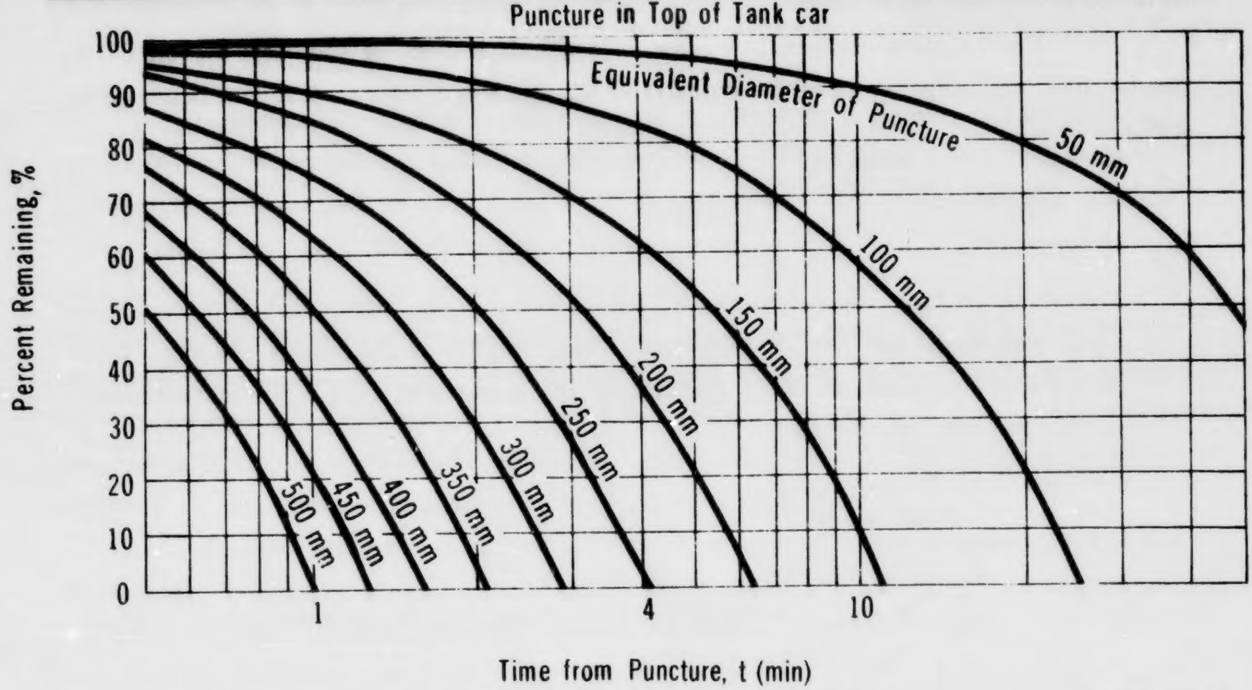
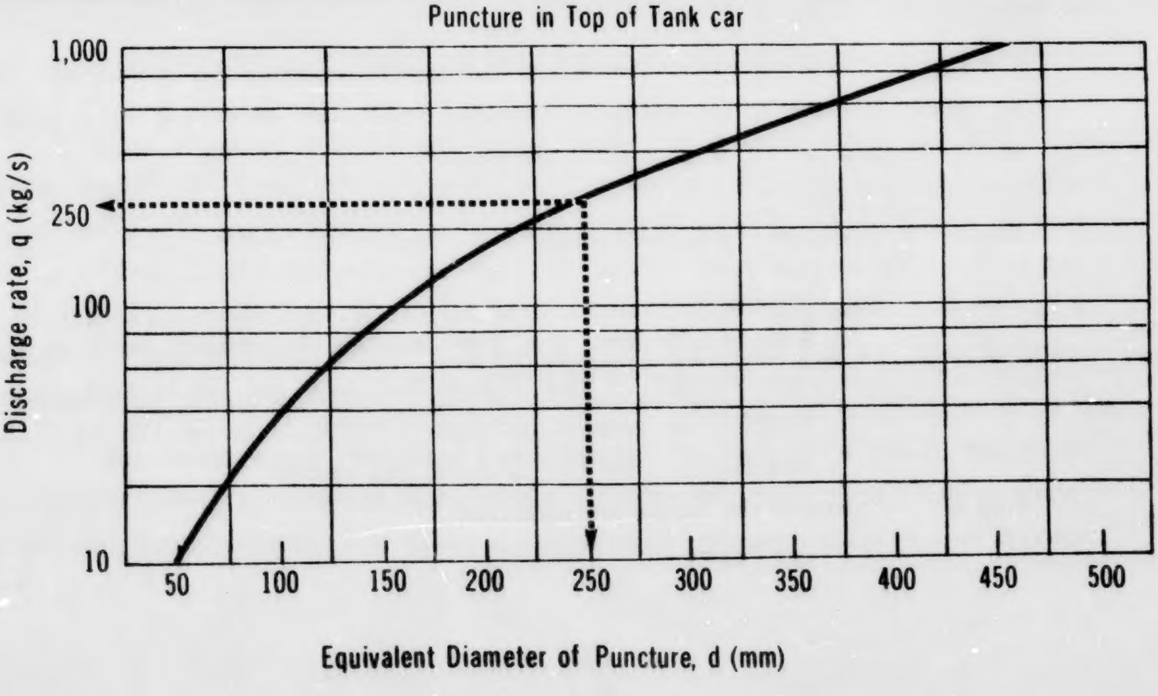


FIGURE 10

HYDROGEN SULPHIDE

DISCHARGE RATE vs PUNCTURE SIZE



venting rate will be constant until all the liquid is vaporized, since the same assumptions as noted above have been made.

The values presented in Figure 10 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 2 900 kPa.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car containing 80 000 L of hydrogen sulphide at 40°C has been punctured on the bottom. The equivalent diameter (d) of the hole is 150 mm. What percent of the initial 80 000 L remains after 0.4 min and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate amount remaining at t = 0.4 min

- Use Figure 7
- With t = 0.4 min and d=150 mm, the amount remaining is about 53 percent or 42 000 L

Step 2: Calculate the discharge rate

- Use Figure 8
- With d=150 mm, the instantaneous discharge rate (q) = 950 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate?

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 9
- With d=250 mm, the tank empties (0 percent remaining) in approximately 4 min (Note: The tank car would still contain 80 000 L of gaseous hydrogen sulphide or about 123 kg of the material until the tank is thoroughly vented)

Step 2: Calculate the vapour emission rate

- Use Figure 10

- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 250 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since liquid hydrogen sulphide is extremely volatile, vapour release from a liquid pool on a ground or water surface will be quite rapid. The pool will boil rapidly and may tend to spread and break up into small globules (popcorn effect). The rate of vapour release is sufficiently high to be considered instantaneous, in the form of a puff, and is the only type of vapour release treated in this manual. It is also pointed out that a constant emission from a blown-out sour gas well, another type of spill situation, will produce a plume that should be of similar shape as that of the puff trace. This vapour release, however, is considered to be continuous. Both plume and puff are generally considered to originate from a point source. The characteristics of the plume will differ significantly from the puff trace and must be calculated separately.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zones, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used in this manual are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 11 depicts schematically the contaminant configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

It is expected that in the initial period immediately after the spill, the hydrogen sulphide cloud will behave as a denser-than-air gas. This is due primarily to the vapour density of hydrogen sulphide gas (1.2 times that of air at 20°C) and due to the fact that the vapour cloud rapidly formed from the spilled liquid will be colder than the surrounding air. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

5.3.2 Vapour Dispersion Nomograms and Tables. The purpose of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

FIGURE 11

SCHEMATIC OF CONTAMINANT PUFF

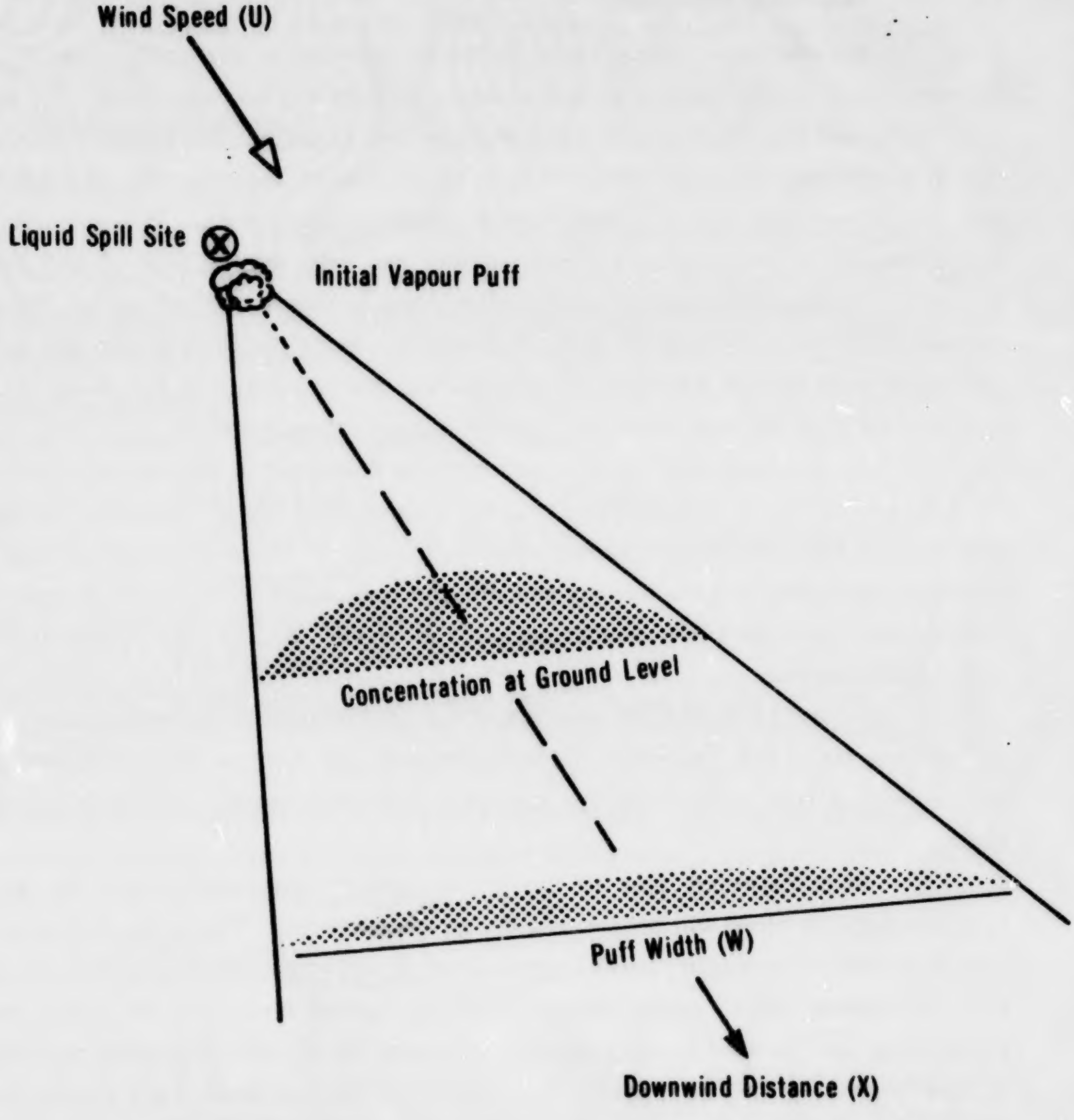

Wind Speed (U)
Liquid Spill Site
Initial Vapour Puff
Concentration at Ground Level
Puff Width (W)
Downwind Distance (X)

Figure 7:	weather conditions
Figure 13:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum puff hazard half-widths
Figure 14:	vapour puff travel distance as a function of travel time elapsed since the spill and wind speed.

The flowchart given in Figure 12 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 13: Normalized vapour concentration versus downwind distance. Figure 13 shows the relationship between the normalized vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud. Condition D is common in most parts of Canada. Before using Figure 13, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

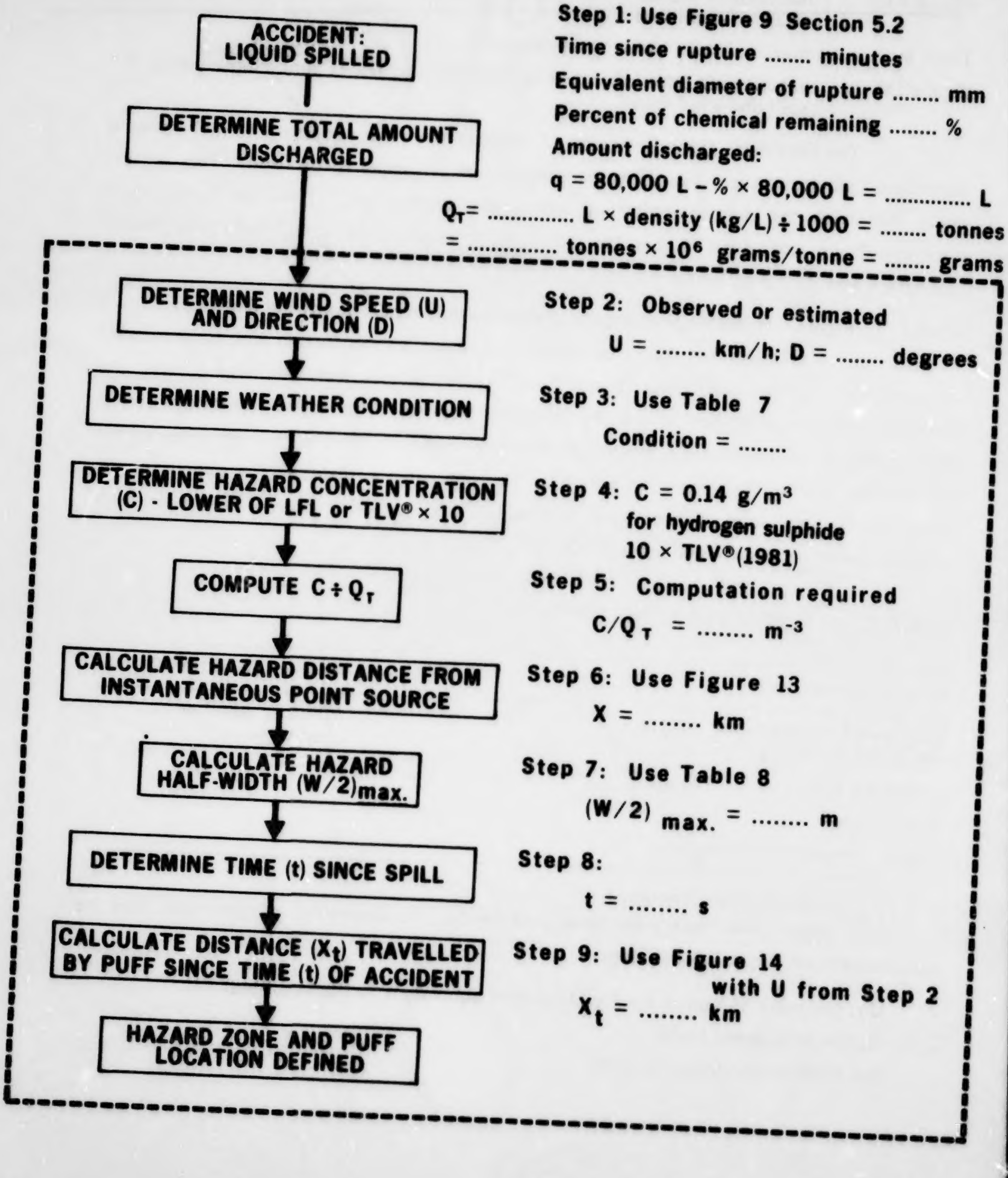
Weather Condition F	Weather Condition D
Wind speed <11 km/h (≈3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	All other weather conditions

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 13 knowing:

- Q_T, the mass of vapour emitted (assumed equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition (D or F)

FIGURE 12

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE


ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C ÷ Q_T
CALCULATE HAZARD DISTANCE FROM INSTANTANEOUS POINT SOURCE
CALCULATE HAZARD HALF-WIDTH (W/2)max.
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (X_t) TRAVELLED BY PUFF SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PUFF LOCATION DEFINED

Step 1: Use Figure 9 Section 5.2

Time since rupture .... minutes

Equivalent diameter of rupture .... mm

Percent of chemical remaining .... %

Amount discharged:

q = 80,000 L − % × 80,000 L = ... L

Q_T = ... L × density (kg/L) ÷ 1000 = ... tonnes

= .... tonnes × 10^6 grams/tonne = ... grams

Step 2: Observed or estimated

U = ... km/h; D = ... degrees

Step 3: Use Table 7

Condition = ...

Step 4: C = 0.14 g/m^3

for hydrogen sulphide

10 × TLV® (1981)

Step 5: Computation required

C/Q_T = ... m^{-3}

Step 6: Use Figure 13

X = ... km

Step 7: Use Table 8

$(W/2)_{max.}$ = ... m

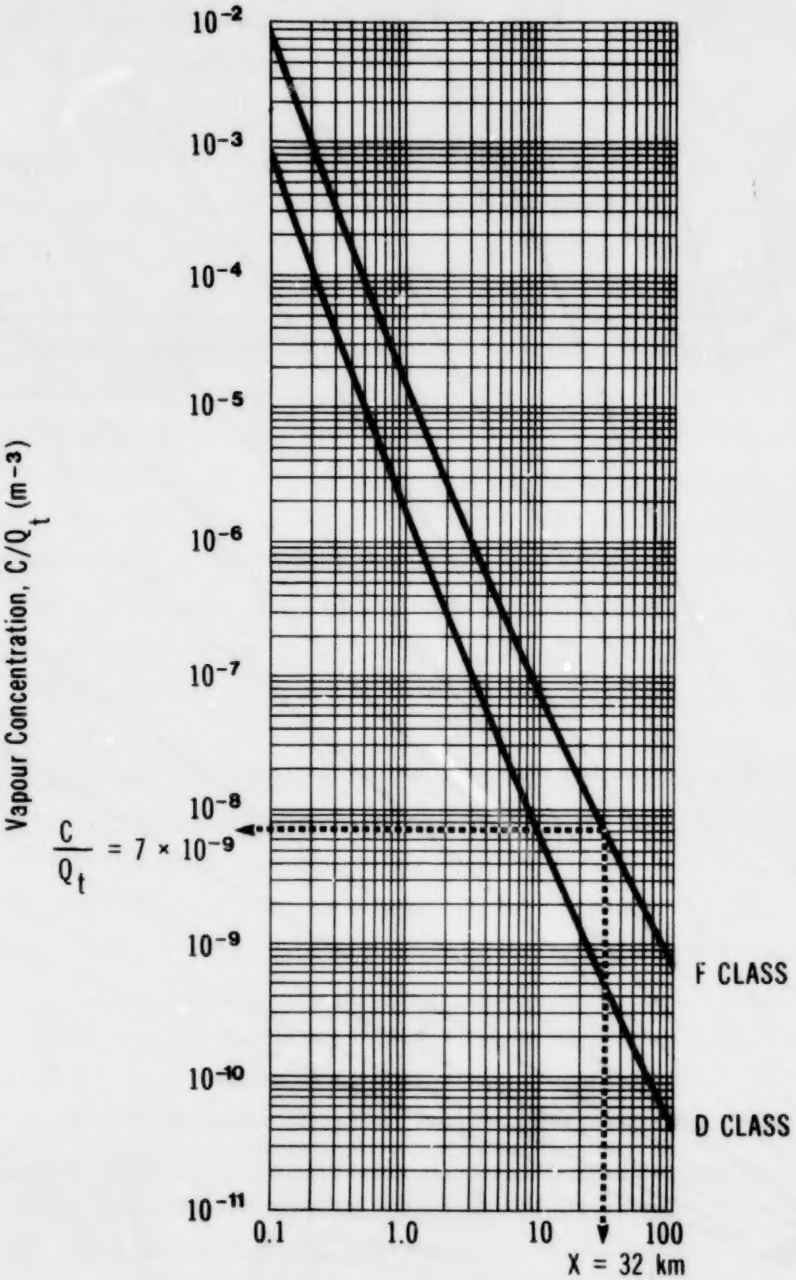
Step 8:

t = ... s

Step 9: Use Figure 14 with U from Step 2

X_t = ... km

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

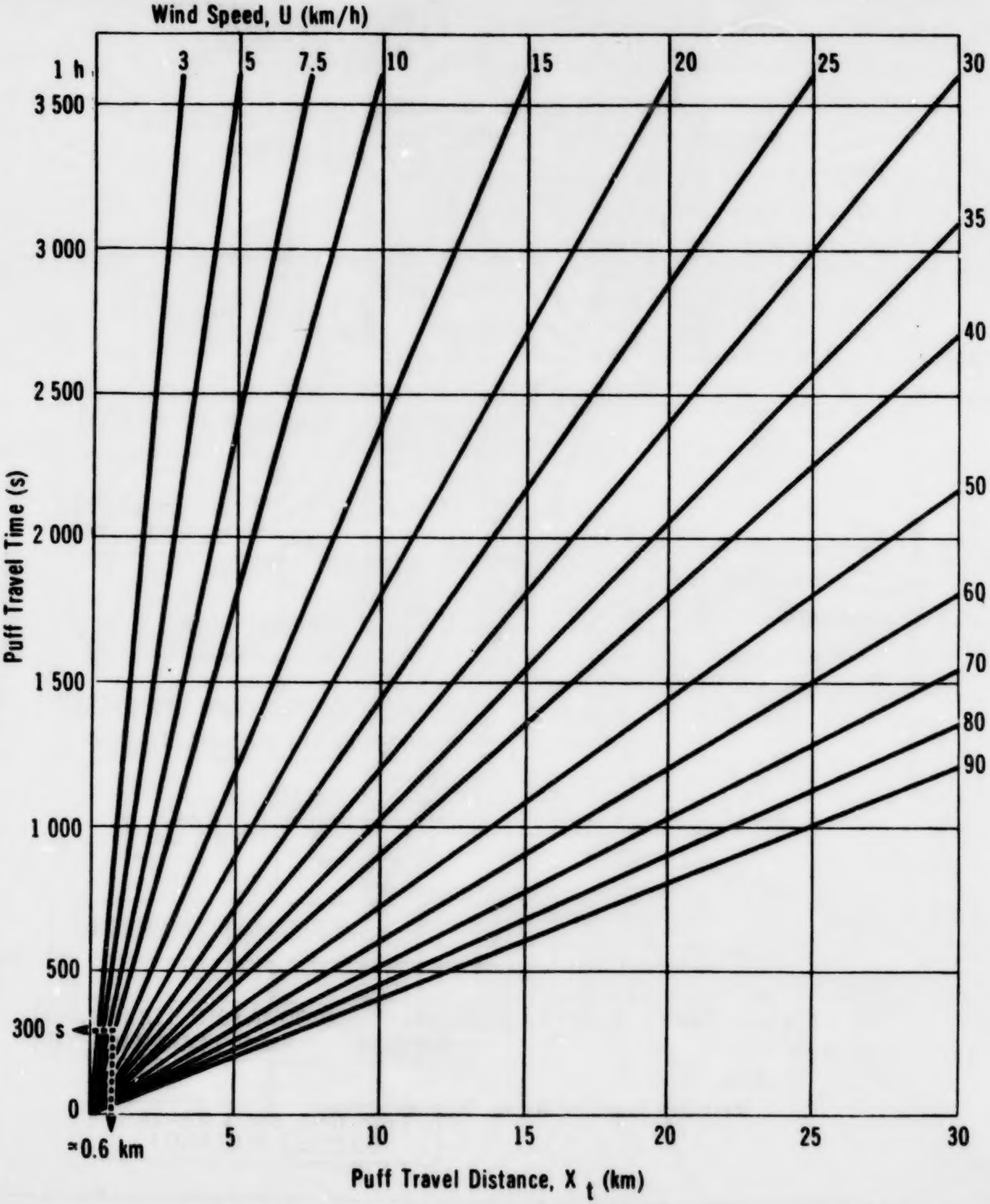


Maximum Downwind Hazard Distance, X (km)

FIGURE 14

HYDROGEN SULPHIDE

PUFF TRAVEL TIME VS TRAVEL DISTANCE



- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value® (TLV in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). (Note: To convert the TLV® (in ppm) and the LFL (in % by volume) to concentrations in g/m^3, use Figures 15 and 16.)

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure; use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.2 **Table 8: Maximum puff hazard half-widths.** This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the hydrogen sulphide Threshold Limit Value (TLV®) of 0.014 g/m^3, or 0.14 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the hydrogen sulphide vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 8 is therefore only applicable for a hydrogen sulphide hazard concentration limit of 10 x TLV®, or 0.14 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

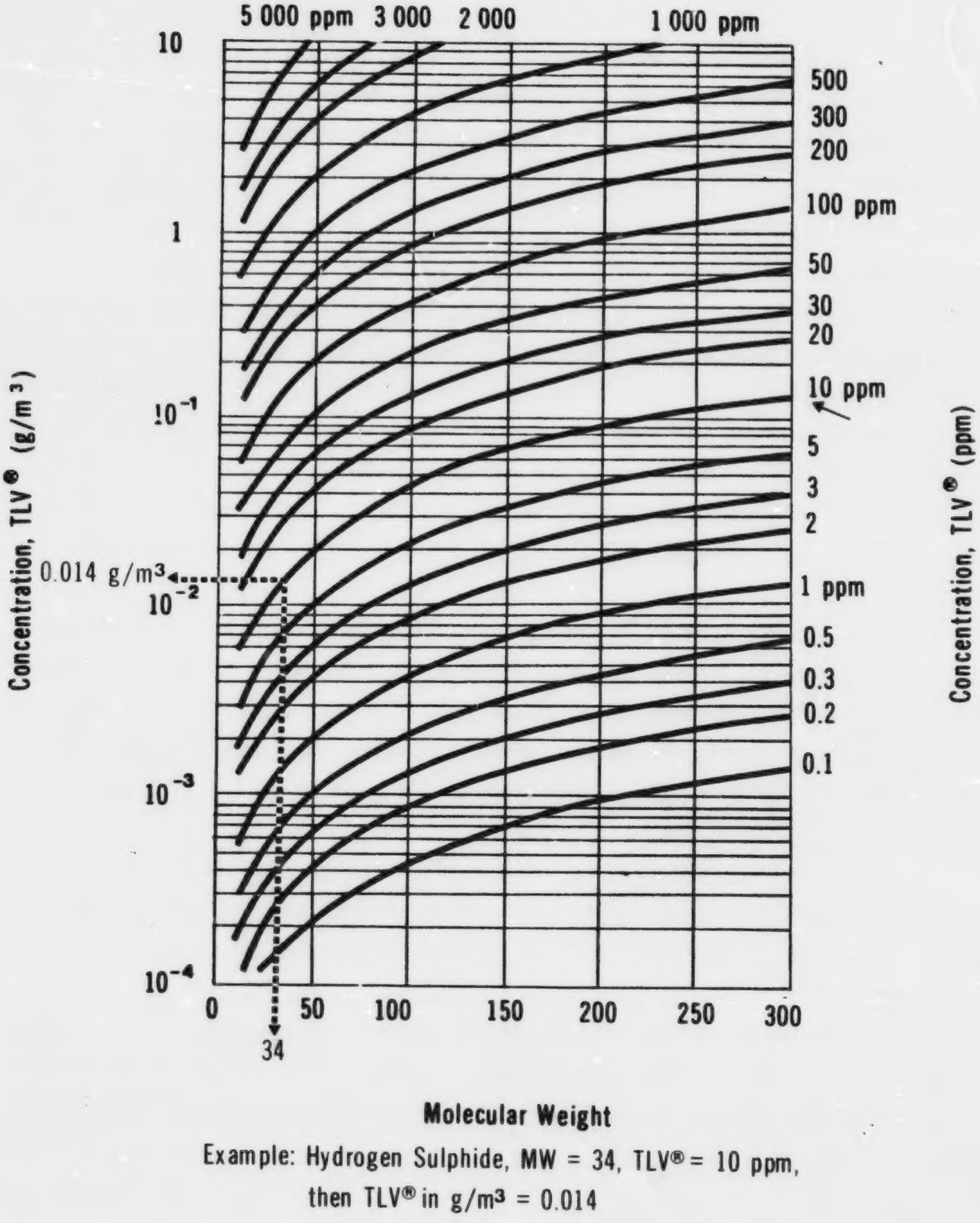
Under weather condition D, the wind speed (U) range applicable is over 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.05 to 4500 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 73 000 kg, or approximately 73 tonnes. In Table 8, under class D, data are provided for up to 61 times this amount, to allow estimation of large spill volumes.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.05 to 200 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 2.75 times a standard rail car load.

Use: Knowing the weather condition and Q_T, one can choose the closest value of Q_T in the table and in turn the corresponding $(W/2)_{max}$, the maximum puff hazard half-width. For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values. An example appears at the bottom of Table 8.

FIGURE 15

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Molecular Weight

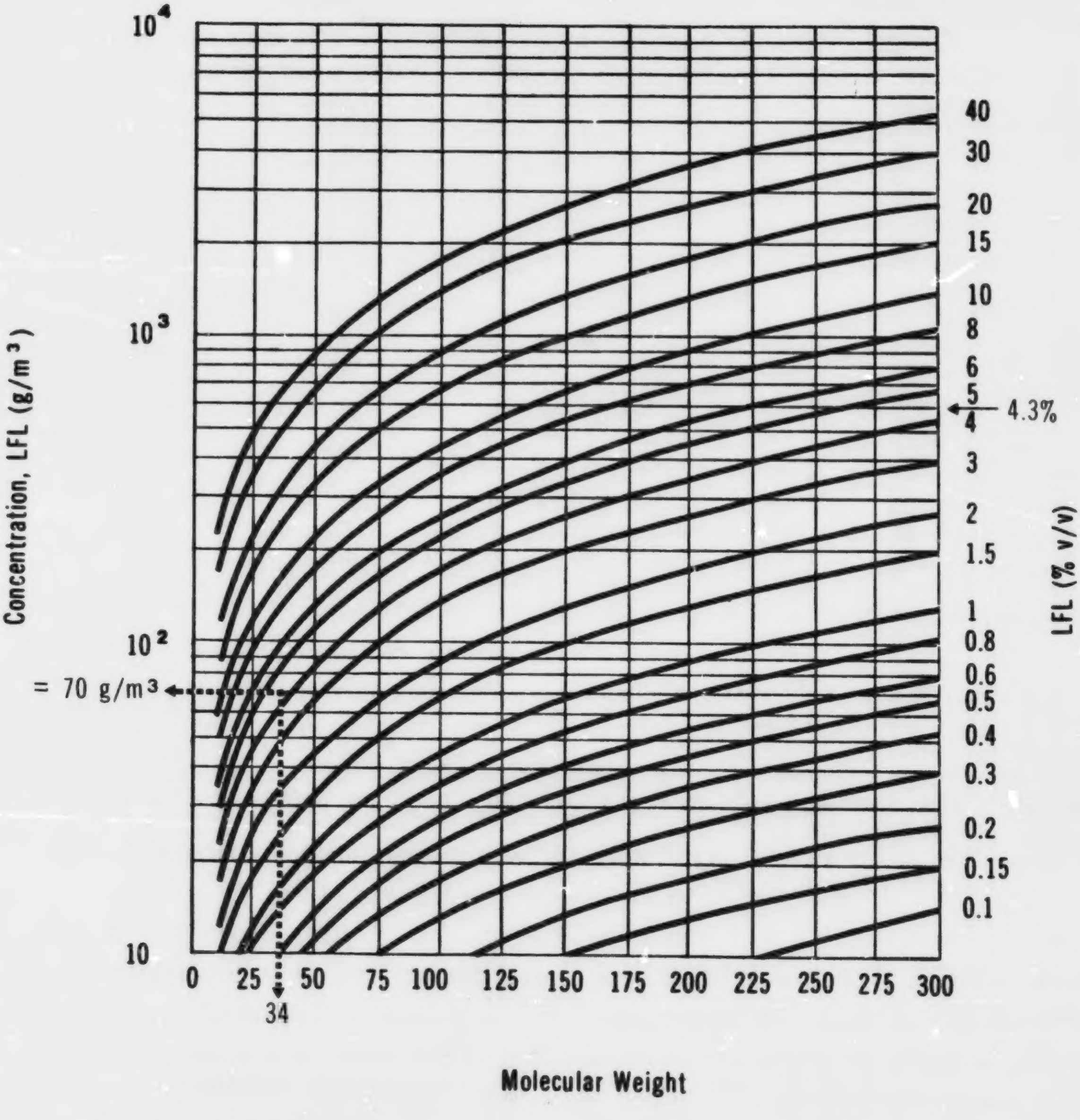
Example: Hydrogen Sulphide, MW = 34, TLV® = 10 ppm,
then TLV® in g/m³ = 0.014

Note: data applicable at 25° and 760 mm Hg pressure

FIGURE 16

HYDROGEN SULPHIDE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Hydrogen Sulphide, MW = 34, LFL = 4.3%,
then LFL in g/m³ = 70

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 8 MAXIMUM PUFF HAZARD HALF-WIDTHS (Hydrogen Sulphide)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
4 500	4 030	($X \leq 99.4$ km)*	200	1 820	($X \leq 97.1$ km)*
4 000	3 850		175	1 720	
3 500	3 660		150	1 610	
3 000	3 450		125	1 490	
2 000	2 950		100	1 355	
1 500	2 645		75	1 200	
1 000	2 265		50	1 010	
750	2 030		25	750	
500	1 740	Q_T = 20 tonnes →	20	680	→ $(W/2)_{max}$ = 680 m
250	1 335		10	510	
200	1 225		7.5	450	
150	1 095		5	385	
100	940		2.5	295	
75	840		1	205	
50	720		0.75	185	
25	565		0.5	155	
20	520		0.25	120	
10	400		0.1	85	
7.5	360		0.05	65	
5	310				
2.5	240				
1	170				
0.5	135				
0.25	105				
0.1	75				
0.05	60				

* Data are provided up to a maximum downwind hazard distance of 100 km

Example: Under weather condition F and Q_T = 20 tonnes, the puff hazard half-width $(W/2)_{max}$ = 680 m

Note: The above table is valid only for a hydrogen sulphide concentration of 10 x TLV®, or 0.14 g/m^3.

5.3.2.3 Figure 14: Puff travel time versus travel distance. Figure 14 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid hydrogen sulphide. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of liquid hydrogen sulphide were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given, $Q_T = 20$ tonnes

- $Q_T = 2 \times 10^7$ g

Step 2: Determine wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: $U = 7.5$ km/h, then $U = 7.5 \div 3.6 = 2.1$ m/s
  $D =$ NW or 315° (D = direction from which wind is blowing)

Step 3: Determine weather condition

- From Table 7, weather condition = F, since U is less than 11 km/h and it is night

Step 4: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL, so for hydrogen sulphide
  $C = 0.14$ g/m^3 (TLV® = 0.014 g/m^3; LFL = 70 g/m^3)

Step 5: Compute C/Q_T

- $$C/Q_T = \frac{0.14}{2 \times 10^7} = 7 \times 10^{-9} \text{ m}^{-3}$$

Step 6: Calculate hazard distance (X) from the instantaneous point source.

- From Figure 13, with $C/Q_T = 7 \times 10^{-9}$ m^{-3} and weather condition F, $X \simeq 32$ km

Step 7: Calculate puff hazard half-width $(W/2)_{max}$

- Use Table 8
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 680 m

Step 8: Determine the time since spill

- t = 5 min x 60 = 300 s

Step 9: Calculate distance travelled (X_t) by vapour puff since time of accident

- Using Figure 14 with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10:

- Map the hazard zone
- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (680 m) by the maximum hazard distance downwind of the instantaneous point source (32 km) along the direction of the wind, as shown in Figure 17
- If the wind is reported to be fluctuating by 20° around 315° (or from 315° ± 10°), the hazard zone is defined as shown Figure 18
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 250 minutes before the puff reaches the maximum downwind hazard distance of 32 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, liquid hydrogen sulphide will spread on the surface, vaporizing rapidly. Hydrogen sulphide is soluble in water and some will inevitably dissolve.

For the purpose of nomogram preparation, two worst case situations have been assumed. First, the extent of spreading on the surface of the water has been estimated, assuming that none of the liquefied hydrogen sulphide is mixed with the water. However, the loss due to vaporization has been taken into account. Secondly, the water pollution has been evaluated by assuming that all of the hydrogen sulphide dissolves in the water and no vaporization occurs. These two cases represent the worst case situations for the extent of spread of hydrogen sulphide on the surface of water and for the water pollution hazard associated with the dissolution of all the liquid hydrogen sulphide.

5.4.2 Spreading on Water. The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since cryogenic liquids such as hydrogen sulphide

FIGURE 17

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

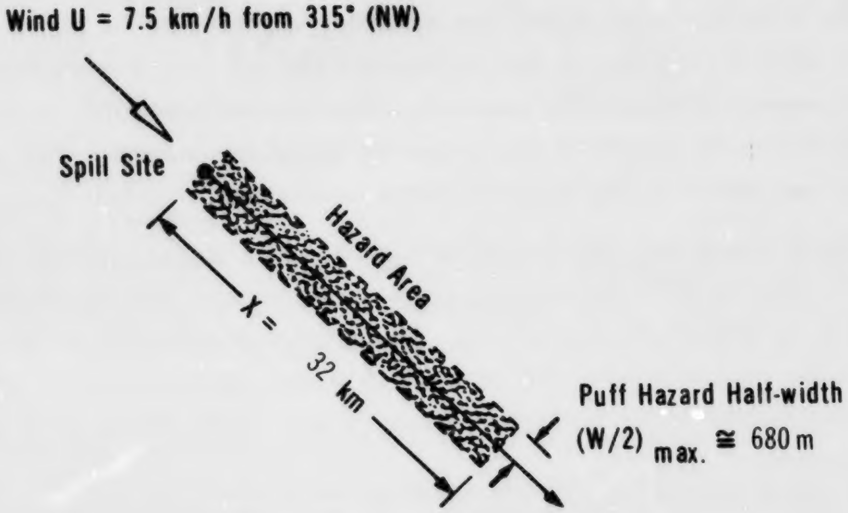
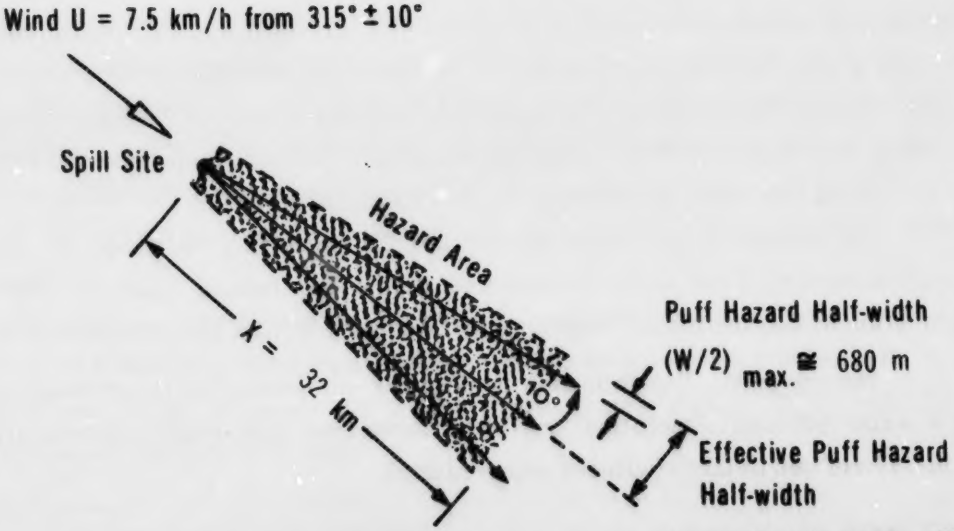

Wind U = 7.5 km/h from 315° (NW)
Spill Site
Hazard Area
X = 32 km
Puff Hazard Half-width
(W/2) max. ≅ 680 m

FIGURE 18

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X = 32 km
10°
Puff Hazard Half-width
(W/2) max. ≅ 680 m
Effective Puff Hazard
Half-width

$= X \times 1000 \times \tan 10° + (W/2)_{max.}$

$= \underline{\ 32\ } \times 1000 \times \tan 10° + \underline{680\ m}$

$= \underline{6320}$ m or 6.3 km

evaporate quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the pool of liquid hydrogen sulphide on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been assumed to be 20°C, representing a reasonable maximum for surface water bodies in Canadian summers. This condition maximizes the spill size. No dissolution is assumed for this case.

5.4.3 Mixing with Water. For this second case, all of the spilled hydrogen sulphide is assumed to dissolve rapidly without any vaporization occurring. Dissolution and mixing take place and the original liquid is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing mechanism is turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. As hydrogen sulphide is less dense than water, the maximum concentration may be near the surface for less turbulent waters.

The one-dimensional model chosen for this manual uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where turbulence and mixing have distributed the dissolved hydrogen sulphide across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d < 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.4 Nomograms. The following nomograms are presented to calculate spreading on still water (without dissolution) and to estimate hydrogen sulphide concentrations in non-tidal rivers and in lakes (without vaporization).

Spreading on Still Water

Figure 19: maximum spill radius versus spill size with estimated times for complete evaporation

Mixing with Water - Non-tidal Rivers

Figure 21: time versus distance for a range of average stream velocities

Figure 22: hydraulic radius versus channel width for a range of stream depths

Figure 23: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 24: alpha* versus diffusion coefficient for various time intervals

Figure 25: alpha versus delta* for a range of spill sizes

Figure 26: maximum concentration versus delta for a range of river cross-sectional areas

Dissolution in Lakes or Still Water Bodies

Figure 27: volume versus radius for the hazard zone for a range of lake depths

Figure 28: average concentration versus volume for the hazard zone for a range of spill sizes

5.4.4.1 Nomogram for spreading on still water.

Figure 19: Maximum spill radius versus spill size. Assuming no dissolution in water, Figure 19 provides a simple means of estimating the maximum spill radius for liquid hydrogen sulphide, if the spill size is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and is based on a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The figures on the nomogram indicated by an arrow provide estimates of the time for complete evaporation of the spill. Because of the relatively short evaporation times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not applicable.

5.4.4.2 Nomograms for dissolution in water - non-tidal rivers. The flow chart in Figure 20 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 21 through 28) are described in the following subsections.

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* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 19

HYDROGEN SULPHIDE

MAXIMUM SPILL RADIUS VS SPILL SIZE

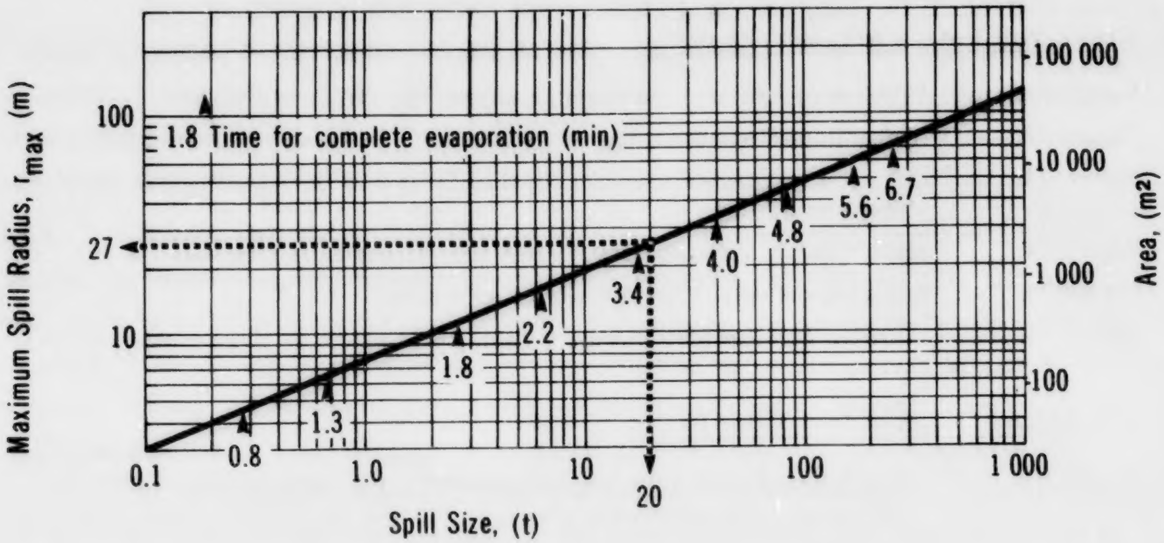


Figure 21: Time versus distance. Figure 21 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 21.

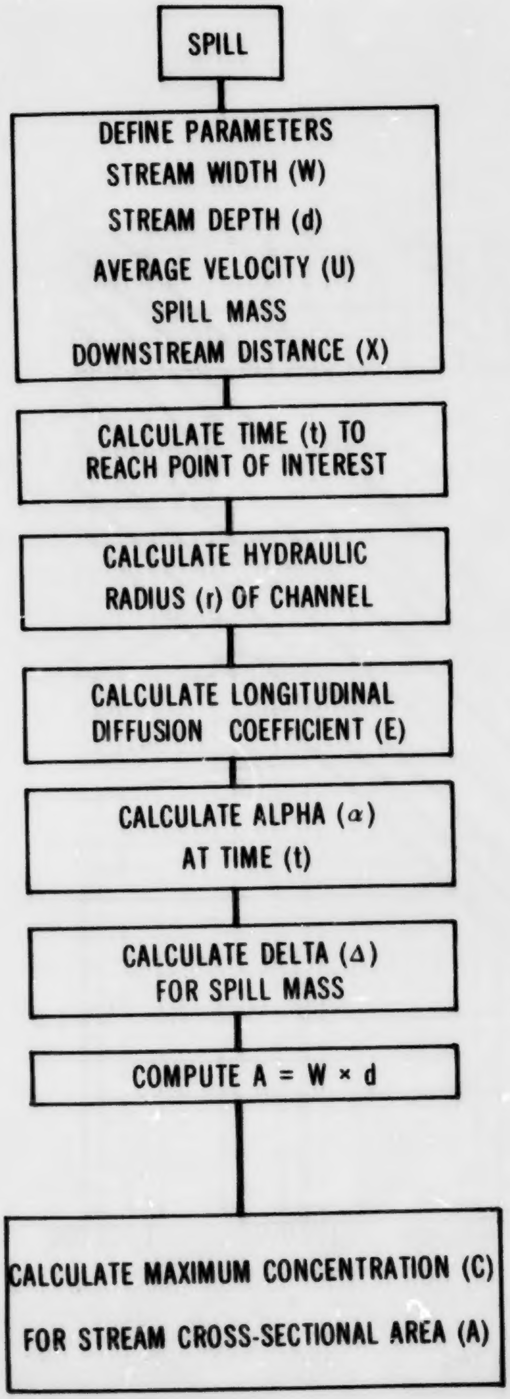
Figure 22: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 22 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 23: Diffusion coefficient versus hydraulic radius. Figure 23 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 22 and the average stream velocity (U).

Figure 24: Alpha versus diffusion coefficient. Figure 24 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

FIGURE 20

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = __________ m

d = __________ m

U = __________ m/s

MASS = __________ tonnes

X = __________ m

Step 2: Use Figure 21

t = __________ minutes

Step 3: Use Figure 22

r = __________ m

Step 4: Use Figure 23

E = __________ m^2/s

Step 5: Use Figure 24

α = __________

Step 6: Use Figure 25

Δ = __________

Step 7: Compute stream cross-sectional Area (A)

$A = W \times d$ _____ m^2

Step 8: Use Figure 26

C = __________ ppm

TIME vs DISTANCE

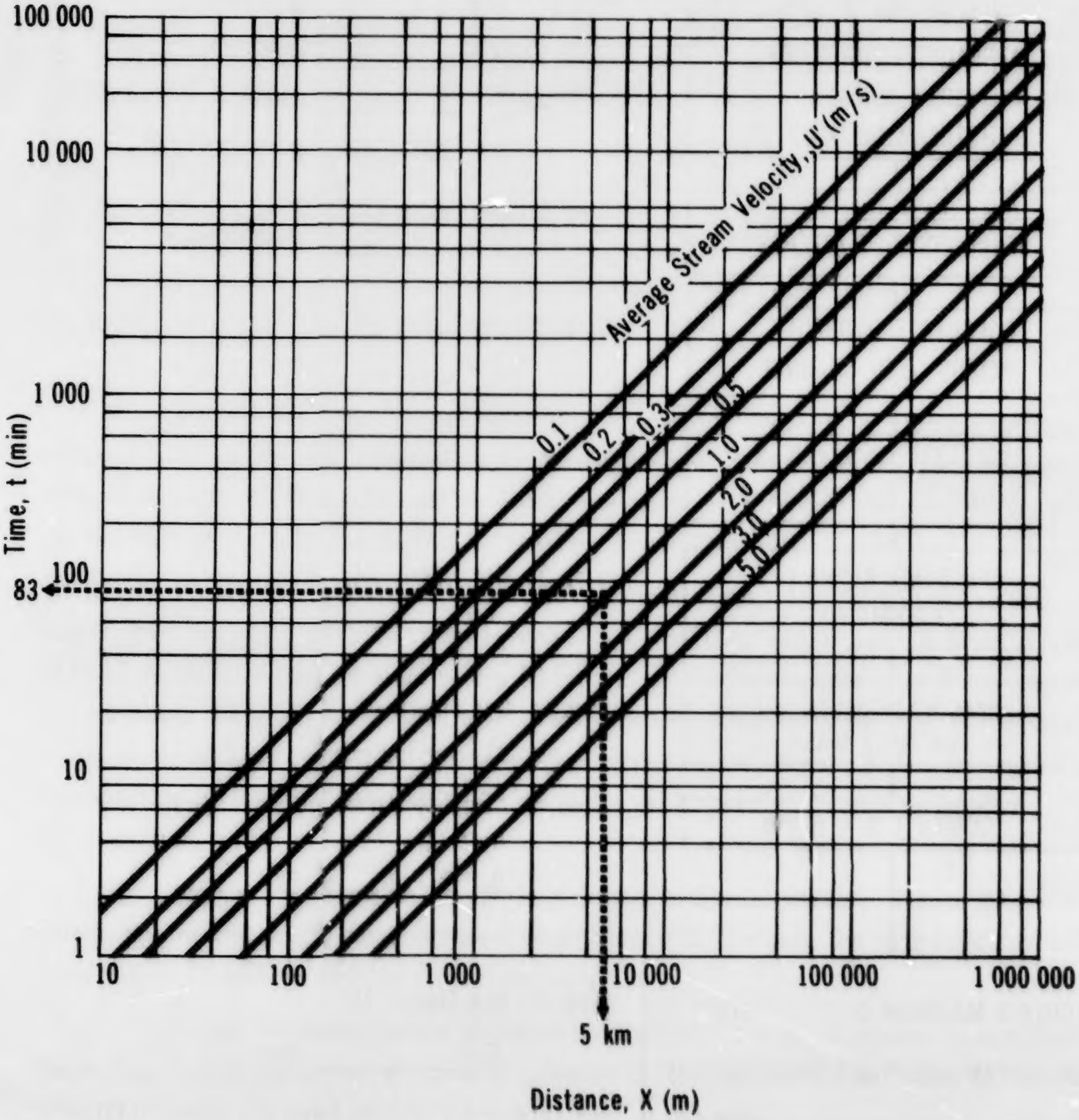
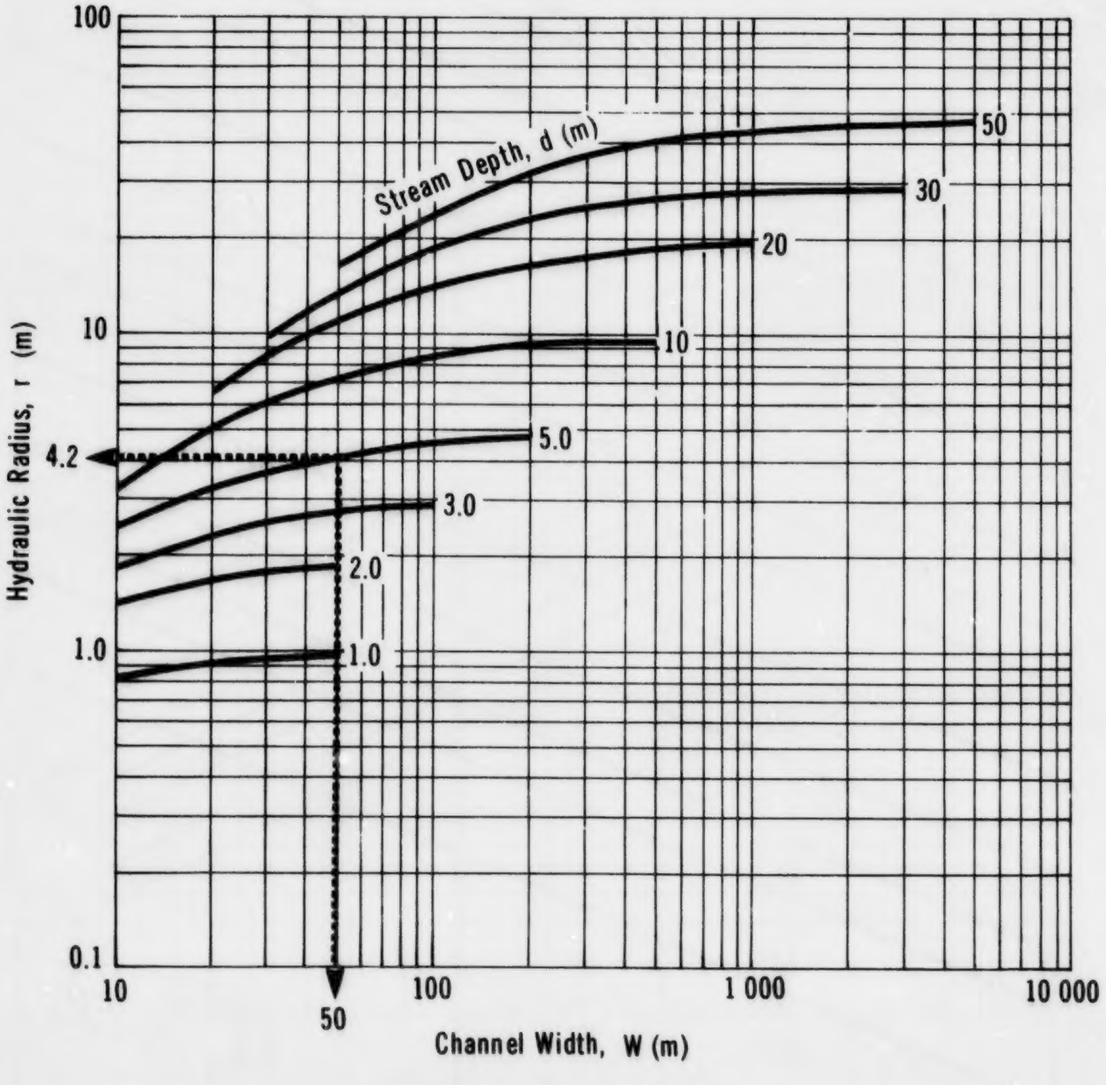
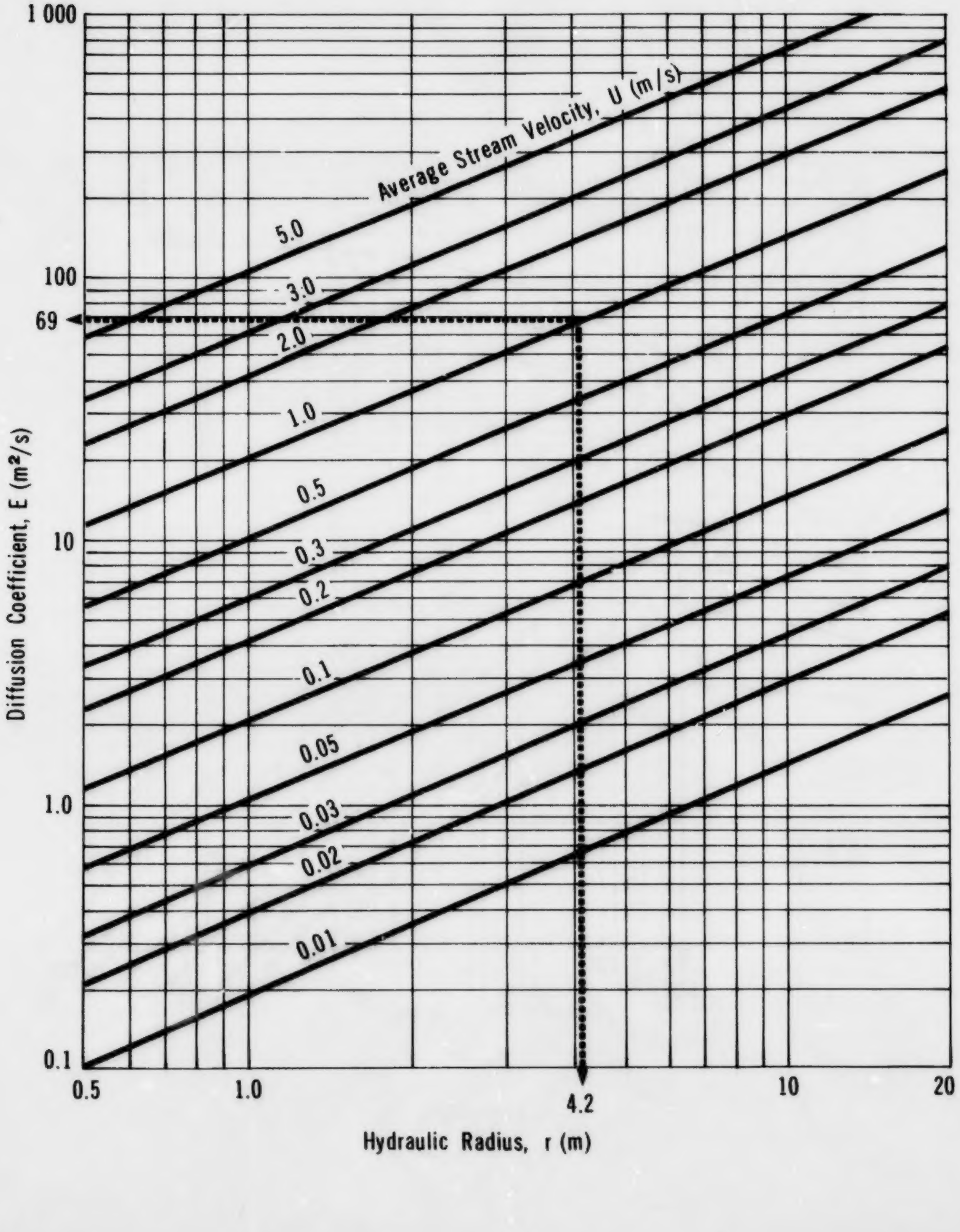


FIGURE 22

HYDRAULIC RADIUS VS CHANNEL WIDTH



DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT

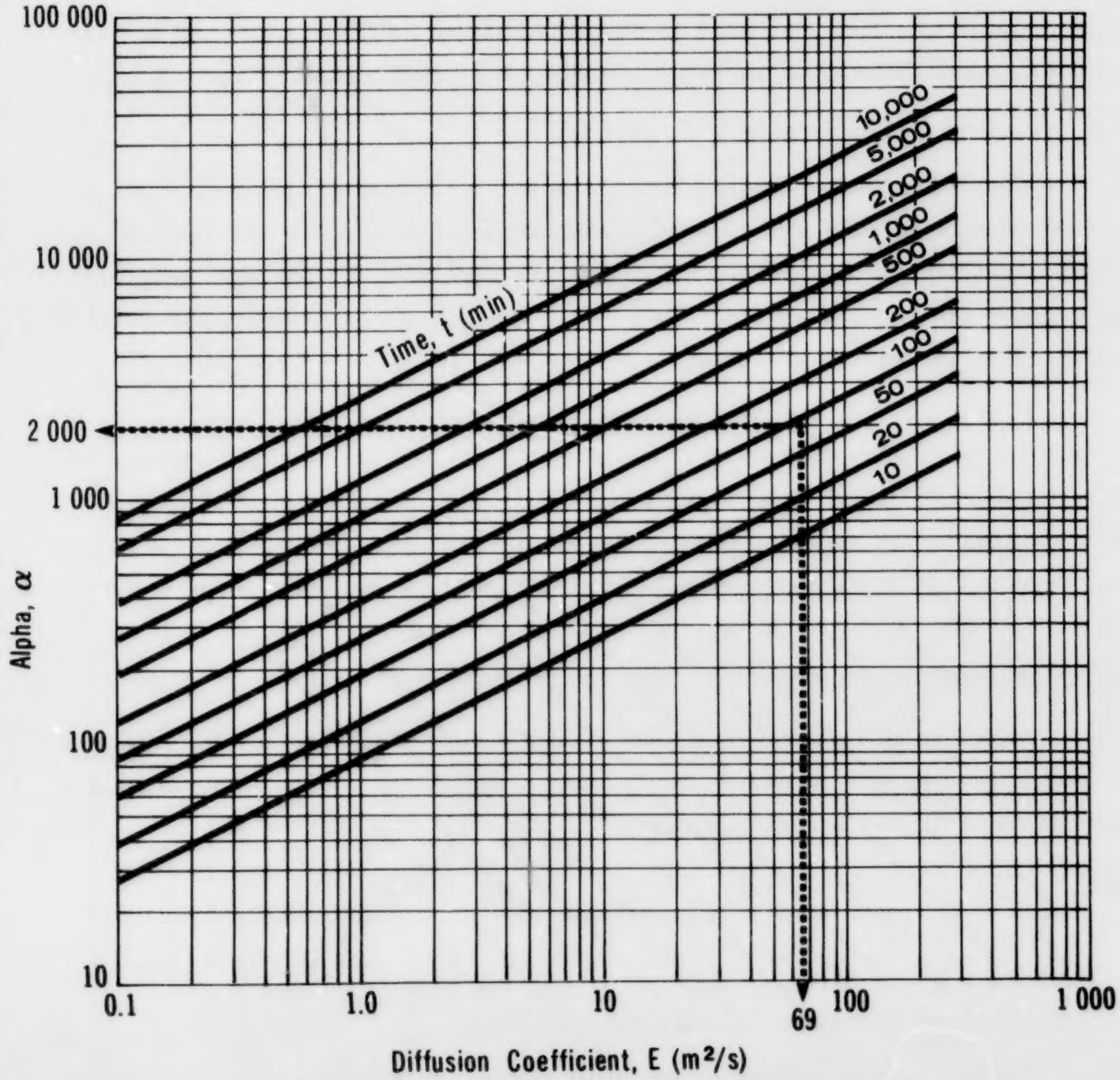


Figure 25: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 25 to allow determination of the hydrogen sulphide concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 26: Maximum concentration versus delta. Figure 26 represents the final step for calculation of the maximum downstream hydrogen sulphide concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration is readily obtained from the nomogram. The value obtained from Figure 26 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.4.3 Nomograms for lakes or still water bodies.

Figure 27: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 27. The radius (r) represents the distance from the spill to the point of interest.

Figure 28: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of hydrogen sulphide (C) can be obtained from Figure 28 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.5 Sample Calculations.

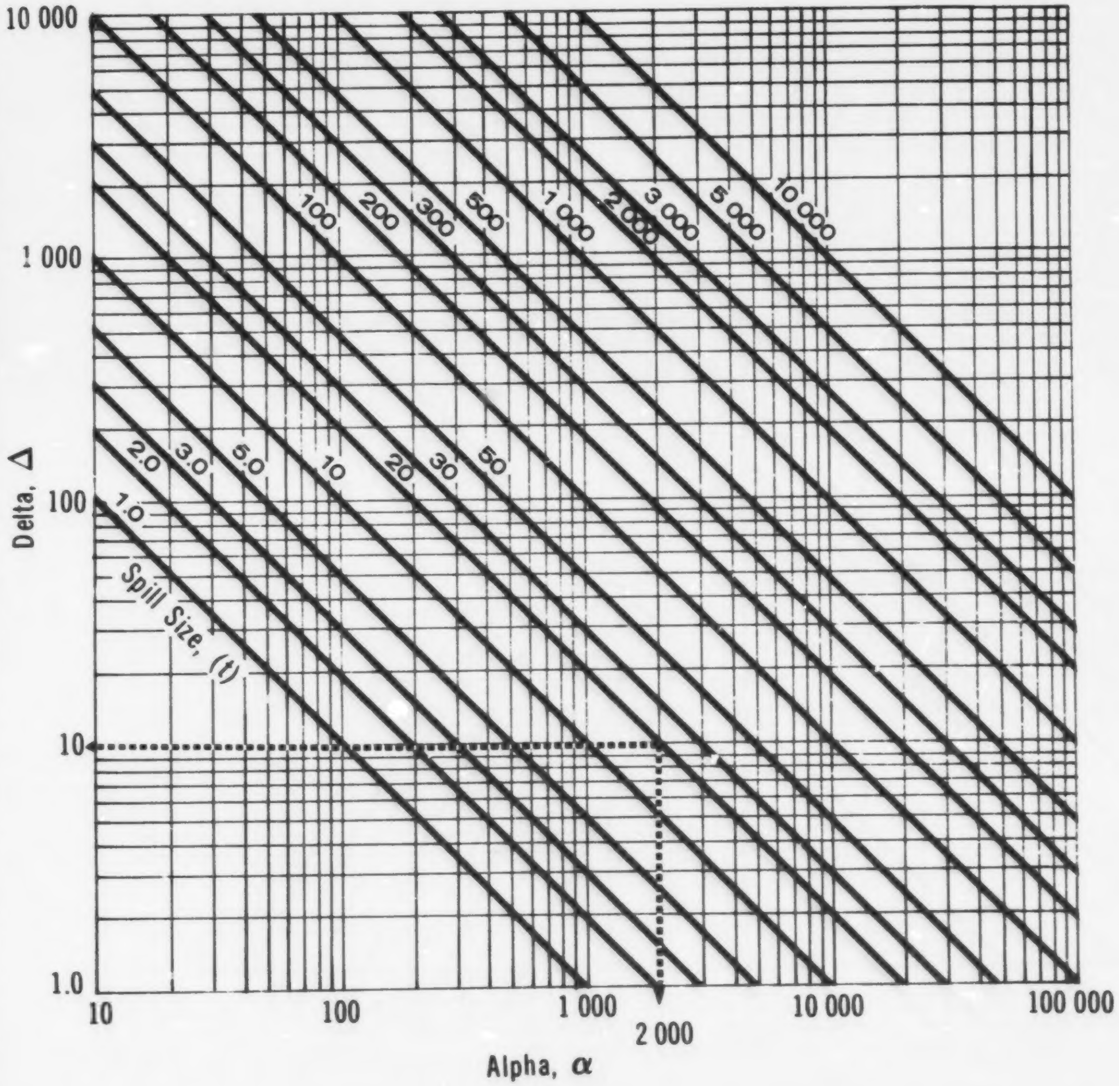
5.4.5.1 Spread on still water. A 20 tonne spill of hydrogen sulphide has occurred on a large lake. What is the maximum radius of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

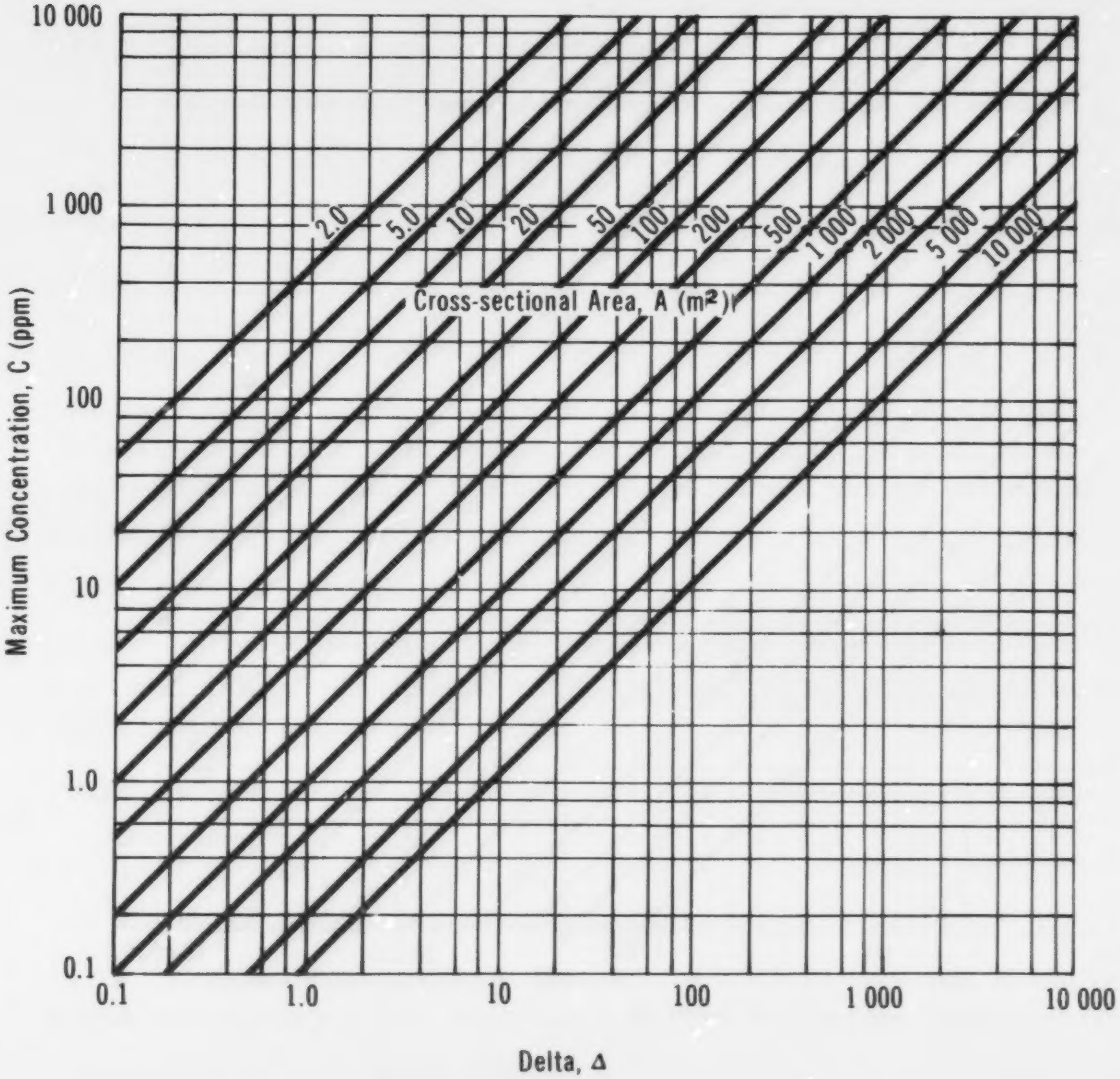
- Use Figure 19
- With mass = 20 tonnes, r_{max} = 27 m
- Time for complete evaporation is a little over 3 min

5.4.5.2 Pollutant concentration in non-tidal rivers. A 20 tonne spill of hydrogen sulphide has occurred in a river. The stream width (W) is 50 m and the stream depth (d) is

ALPHA vs DELTA



MAXIMUM CONCENTRATION vs DELTA



VOLUME vs RADIUS

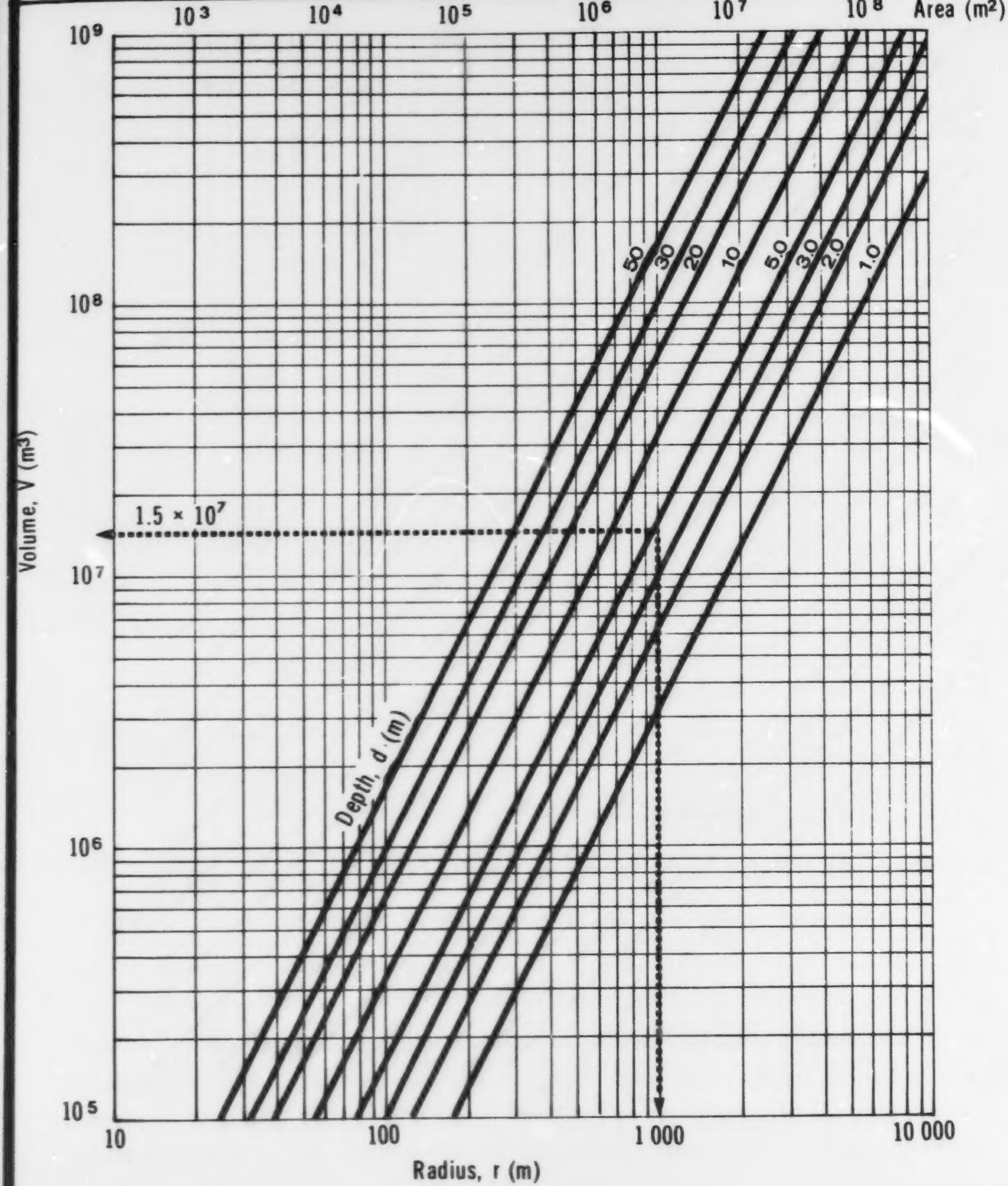
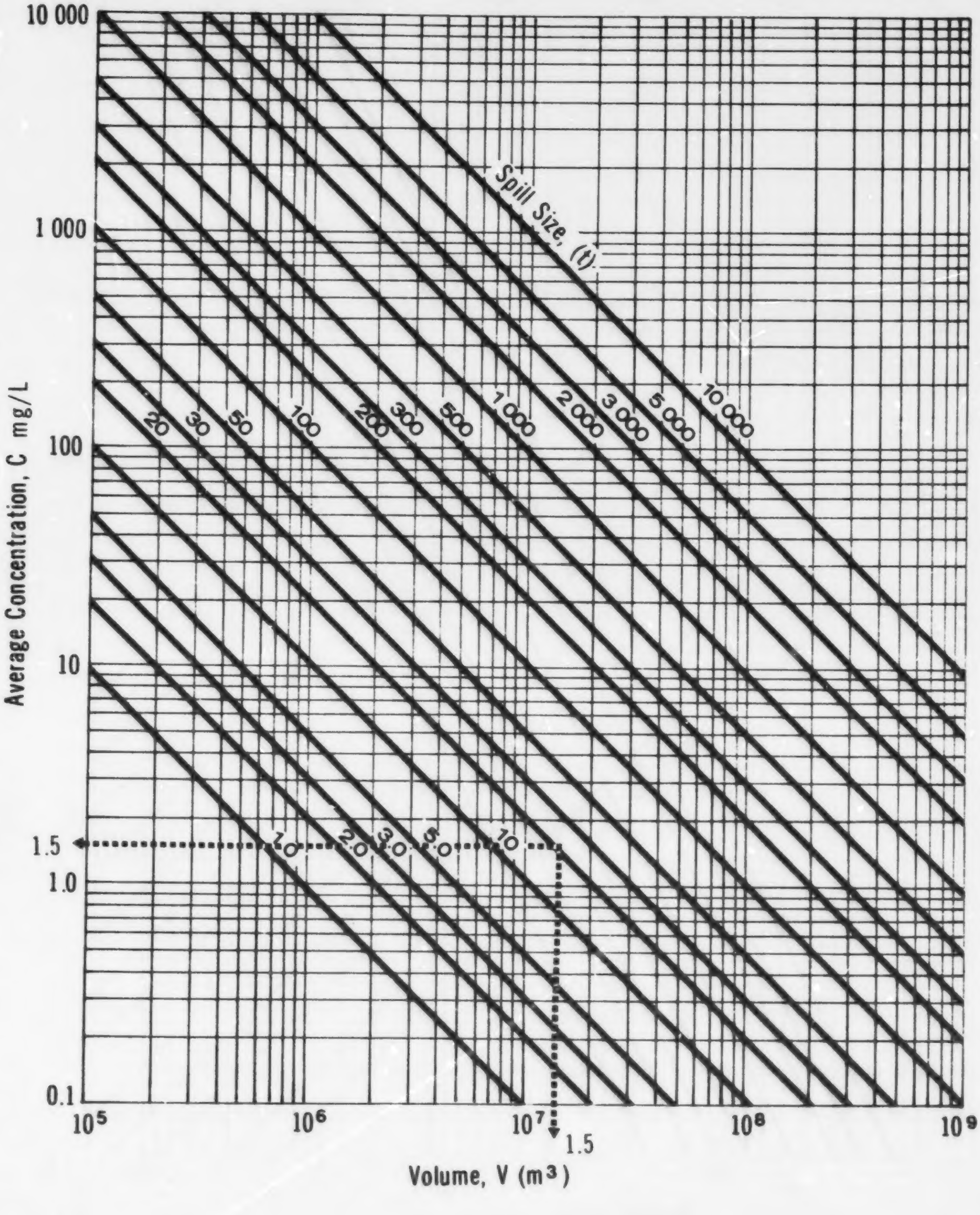


FIGURE 28

HYDROGEN SULPHIDE

AVERAGE CONCENTRATION vs VOLUME



5 m. The average stream velocity (U) is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- $W = 50$ m
- $d = 5$ m
- $U = 1$ m/s
- mass = 20 tonnes
- $X = 5000$ m

Step 2: Calculate time to reach point of interest

- Use Figure 21
- With $X = 5000$ m and $U = 1$ m/s, $t = 83$ min

Step 3: Calculate hydraulic radius (r)

- Use Figure 22
- With $W = 50$ m and $d = 5$ m, $r = 4.2$ m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 23
- With $r = 4.2$ m and $U = 1$ m/s, $E = 69\ m^2/s$

Step 5: Calculate alpha (α)

- Use Figure 24
- With $E = 69\ m^2/s$ and $t = 83$ min, $\alpha = 2000$

Step 6: Calculate delta (Δ)

- Use Figure 25
- With alpha (α) = 2000 and mass = 20 tonnes, delta (Δ) = 10

Step 7: Compute stream cross-sectional area (A)

- $A = W \times d = 50 \times 5 = 250\ m^2$

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 26
- With $\Delta = 10$ and $A = 250\ m^2$, $C = 45$ ppm ($64\ mg/m^3$)

5.4.5.3 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of hydrogen sulphide has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- $d = 5$ m
- $r = 1000$ m
- mass = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 27
- With $r = 1000$ m, $d = 5$ m, the volume is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 28
- With $V = 1.5 \times 10^7$ m^3 and mass = 20 tonnes, the average concentration (C) is 1.5 mg/L

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this manual are presented in the Introduction Manual. Special considerations related to the spill of hydrogen sulphide onto soil and the transport downward through the soil are presented in this section.

Anhydrous hydrogen sulphide has a boiling point of -60.7°C at 1 atmosphere. When spilled onto soil, the extremely volatile liquid will boil vigorously and vaporize rapidly. This process will be accompanied by bumping and possibly by the formation of small globules. Since hydrogen sulphide is quite soluble in water, the presence of water in the soil or as precipitation at the time of the spill may facilitate downward movement in the soil. If, however, the soil is saturated with water, as might be expected after a heavy rainfall, the spilled liquid will probably not be transported downward. It will boil rapidly, flow to the lowest point and dissolve to some extent. Downward transport will only occur if the general movement of the water is toward the water table through the pore spaces of the unsaturated zone. The unsaturated zone is defined as that zone immediately above the water table where the soil pore spaces are only partially filled with water. If the zone is saturated, there will be virtually no movement of dissolved hydrogen sulphide toward the groundwater (unconfined aquifer).

For the purposes of this manual, the three types of soil have been assumed to be at field capacity. This situation provides very little interstitial water in the unsaturated zone to dilute the neat spilled material or aqueous solutions thereof during downward transport or to impede its downward movement. This represents a "worst case" analysis. In addition, it is assumed that a significant portion of the spilled liquid hydrogen sulphide has dissolved in water introduced by external sources such as precipitation, fire-fighting, vapour knock-down, etc. The downward moving liquid for this manual, therefore, is water contaminated with dissolved hydrogen sulphide. Since the dissolved hydrogen sulphide is not expected to significantly change the viscosity and density of the water, the values for those particular properties of pure water will be used for this problem.

Some of the aqueous hydrogen sulphide may react chemically with soil materials during downward transport, especially in carbonate-based (limestone) soils. Since aqueous hydrogen sulphide behaves as a weak acid, it will react with the mildly basic solution resulting from the hydrolysis of the aqueous carbonate ion. Since the material under discussion is relatively soluble in water, a significant amount may move downward toward the water table. For simplicity, this analysis does not take chemical interaction factors into consideration.

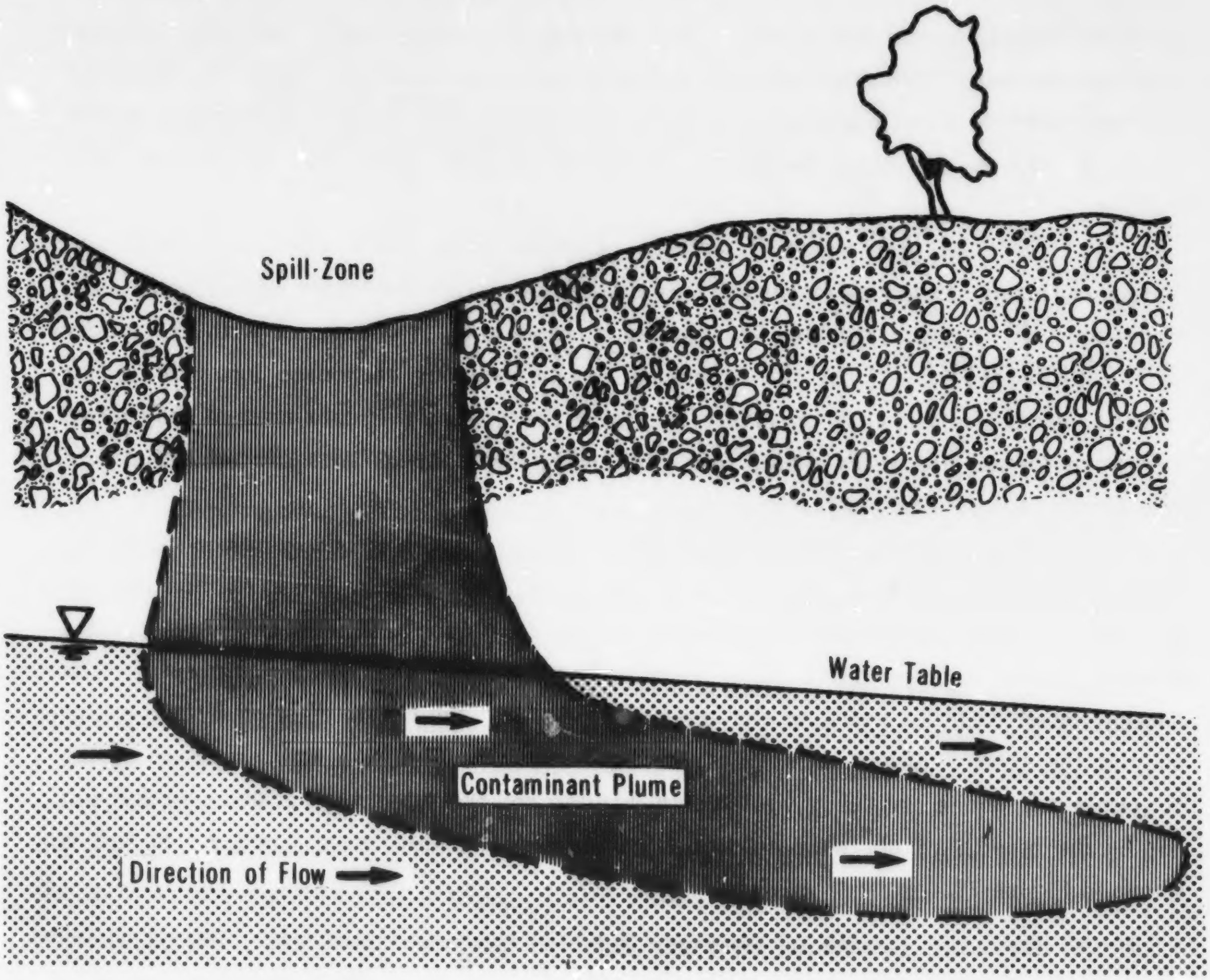
Upon reaching the water table and entering the groundwater system, the hydrogen sulphide solution will continue to move, but now in the direction of the groundwater flow. A contaminated plume will develop which will generally move along a definite route controlled by head relationships within the aquifer system. The contaminated material entering the groundwater is not subject to dilution by the entire body of the groundwater system. Factors influencing the diffusion and dispersion of the contaminated plume are fairly well known, but are not the subject of this manual and will not be discussed further. A simplified schematic of the downward transport in soil is shown in Figure 29.

5.5.2 Equations Describing Hydrogen Sulphide Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Hydrogen Sulphide Movement into Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

SCHEMATIC SOIL TRANSPORT


Spill-Zone
Water Table
Contaminant Plume
Direction of Flow

Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

where k = intrinsic permeability of the soil (m^2)
ρ = mass density of the fluid (kg/m^3)
μ = absolute viscosity of the fluid (Pa•s)
g = acceleration due to gravity = $9.81\ m/s^2$

Property	Hydrogen Sulphide, 20°C	Water, 20°C
Mass density (ρ), kg/m^3	774	1000
Absolute viscosity (μ), Pa•s	N/A	1.0×10^{-3}
Saturated hydraulic conductivity (K_o)	N/A	$(0.98 \times 10^7)k$

5.5.4 **Soils.** The Introduction Manual describes the three soils selected tor this work. Their relevant properties are:

Property	Soil Type Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 **Penetration Nomograms.** Nomograms for the penetration of hydrogen sulphide solutions into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p. A flowchart of the use of the nomograms is presented in Figure 30. The nomograms are presented as Figures 31, 32 and 33.

5.5.6 **Sample Calculation.** A 20 tonne spill of hydrogen sulphide has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. The groundwater table depth has been determined to be 13 m. Calculate the depth of penetration 15 minutes after the spill.

FIGURE 30

FLOWCHART FOR NOMOGRAM USE

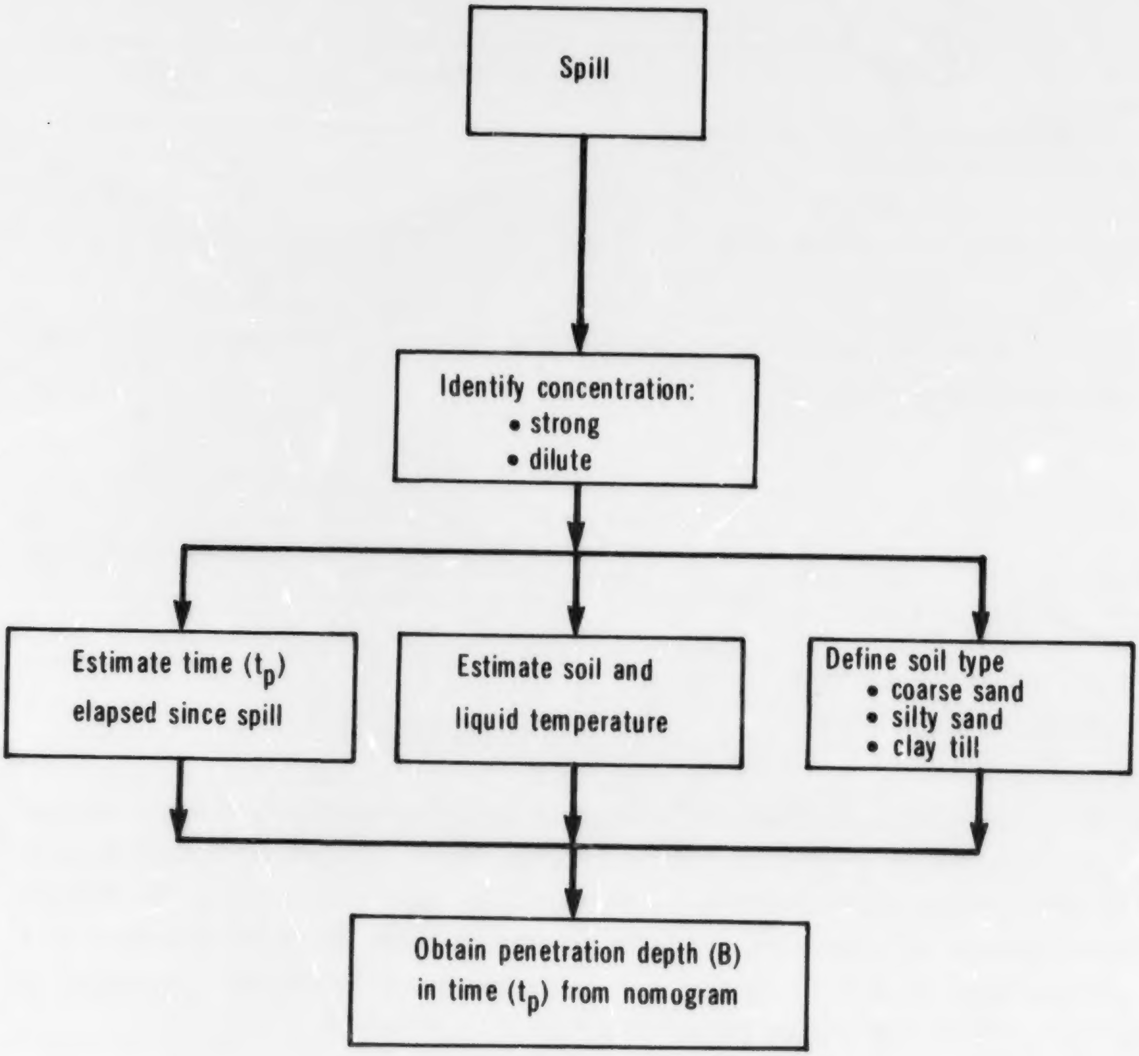

Spill
Identify concentration:
• strong
• dilute
Estimate time (t_p) elapsed since spill
Estimate soil and liquid temperature
Define soil type
• coarse sand
• silty sand
• clay till
Obtain penetration depth (B) in time (t_p) from nomogram

FIGURE 31

PENETRATION IN COARSE SAND

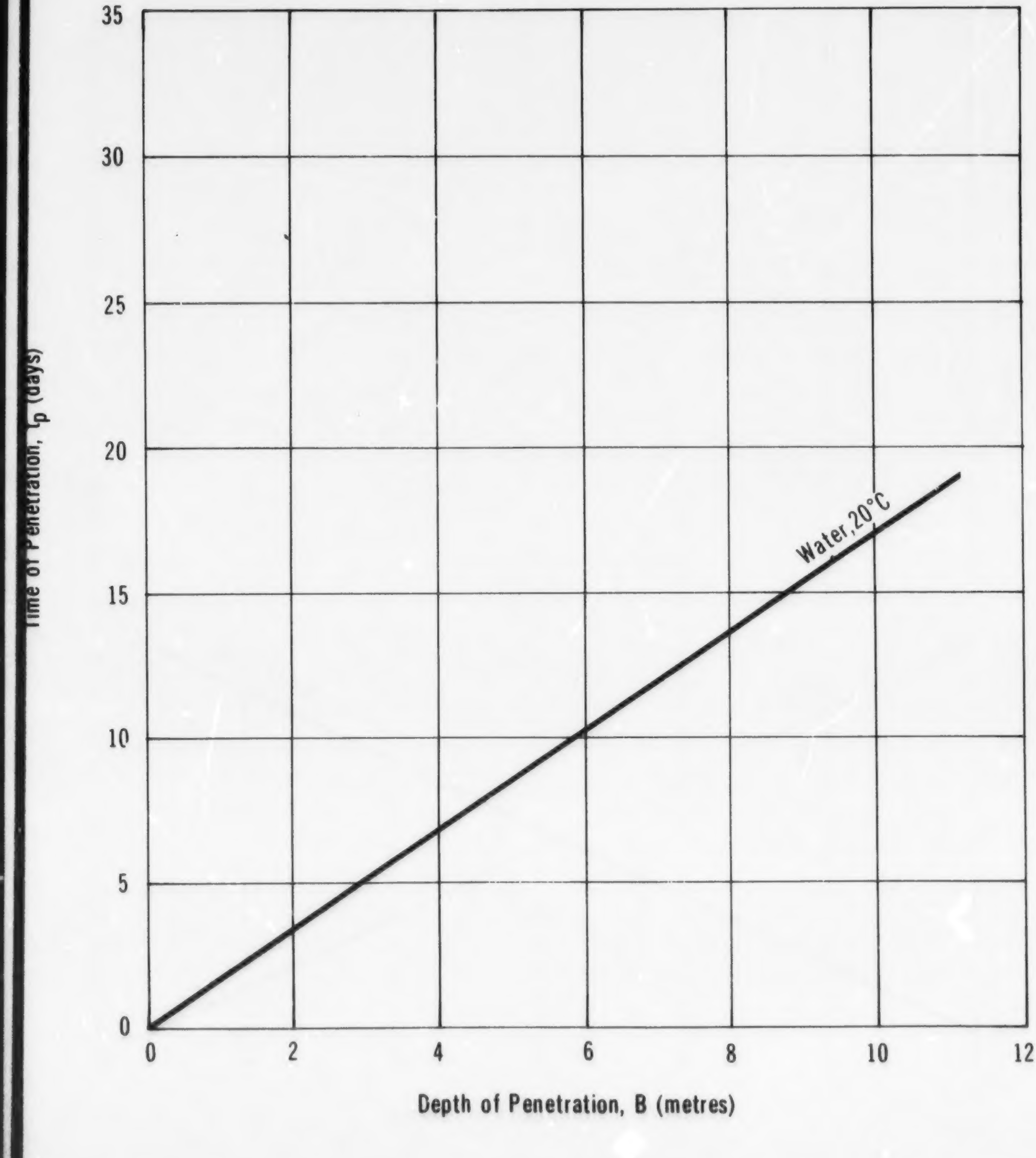
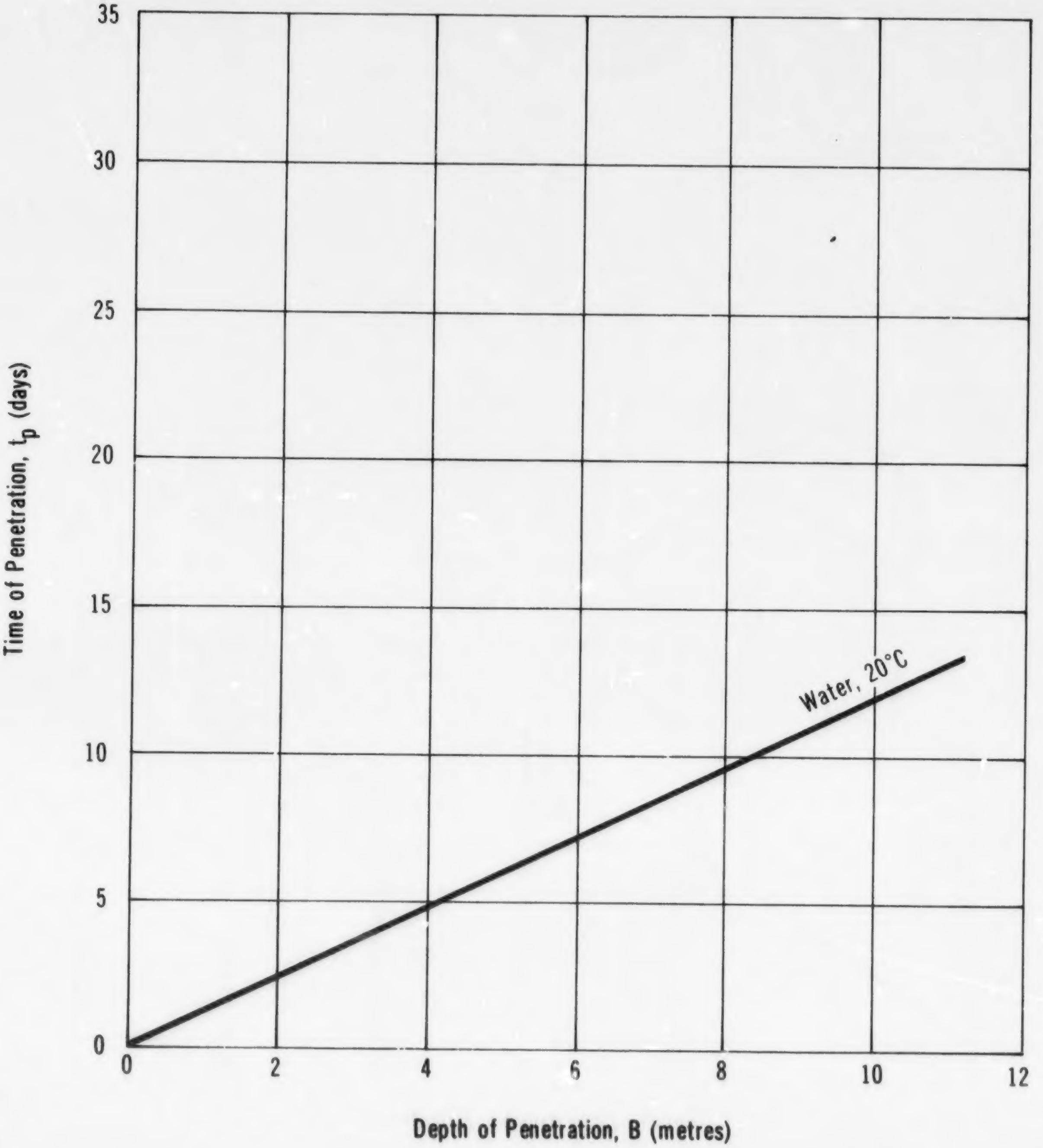
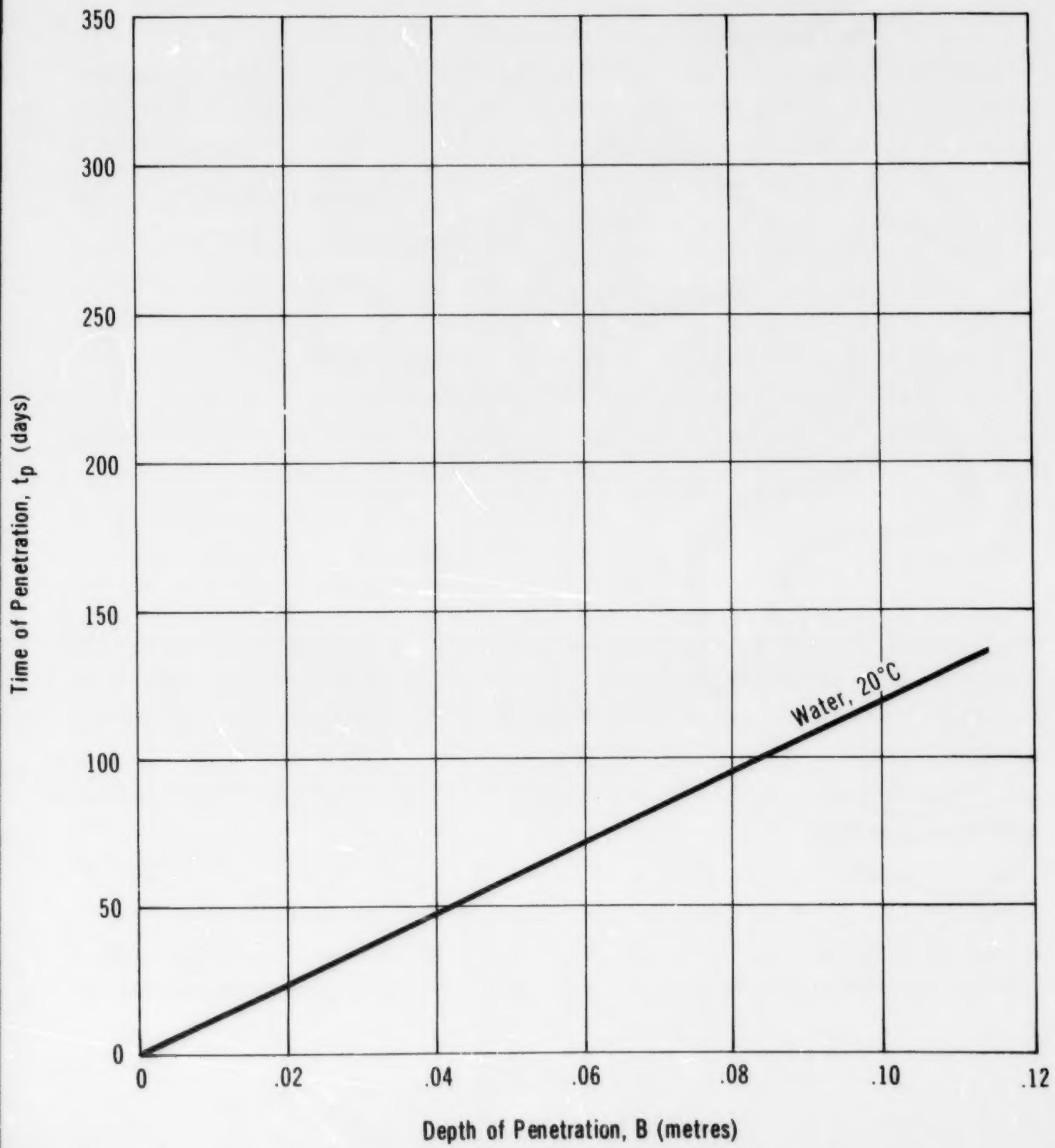


FIGURE 32

PENETRATION IN SILTY SAND



PENETRATION IN CLAY TILL



Solution:

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- $r = 8.6$ m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 15 min

Step 2: Calculate area of spill

- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Estimate depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.8 m at t_p = 15 min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. The Canadian drinking water limit for sulphides is 0.05 mg/L (Guidelines/Canadian/Water 1978).

6.1.2 Air. New Brunswick's maximum permissible ground level concentration for hydrogen sulphide is 15 $\mu g/m^3$ (N.B. Clean Environment Act 1973). Ontario's limit is 30 $\mu g/m^3$ (Ontario E.P. Act 1971). Alberta permits the long-term presence of 4 $\mu g/m^3$ (Kirk-Othmer 1983).

6.2 Aquatic Toxicity

6.2.1 Toxicity Rating. It is well known that hydrogen sulphide is a characteristic of oil and gas deposits and is associated with groundwaters. It may also be formed under anaerobic conditions in lakes. The toxicity of sulphide solutions has been shown to increase as the pH of the solutions is lowered. Since hydrogen sulphide dissolved in water behaves as a weak acid, lowering of the pH in a sulphide solution would tend to drive each equation to the left.

$$H_2S \rightleftharpoons HS^- + H^+$$
$$HS^- \rightleftharpoons S^= + H^+$$

In other words, the concentration of undissociated hydrogen sulphide will increase; it can be assumed that the toxicity is primarily due to the hydrogen sulphide molecule. For example, in water containing 3.2 ppm of sodium sulphide (Na_2S), trout overturned in 2 h at pH 9.0, in 10 min at pH 7.8 and in 4 min at pH 6.0. It has been reported that the maximum possible safe level of hydrogen sulphide for *Esox lucius* eggs is between 0.014 and 0.018 ppm, and for *Esox lucius* sac fry is between 0.004 and 0.006 ppm for a 96-h exposure (NRCC 1977).

No U.S. aquatic toxicity rating has been assigned (RTECS 1979). Other references list the threshold concentration for both fresh and and saltwater fish as 0.5 ppm and the chronic aquatic toxicity limit as 0.3 ppm (OHM-TADS 1981; Sax 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	References
Fish Kill Data					
100	3	Tench	toxic	tap water	Verschueren 1977
0.797	48	Catfish	lethal	lake	Bonn 1967
0.86	24	Trout	toxic		WQC 1963
5 to 6	24	Minnows	toxic		WQC 1963
1	not stated	King salmon	toxic		WQC 1963
3.3	24	Carp	toxic		WQC 1963
4.9 to 5.3	1	Sunfish	toxic		WQC 1963
10	96	Goldfish	toxic	hard	WQC 1963
4.3	24	Goldfish	toxic		WQC 1963
Fish Toxicity Tests					
0.007	96	Brown trout	TL_m		Spehar 1981
0.037 ppm	96	Northern pike eggs	LC_{50}	as H_2S	NRCC 1977
0.014 ppm	96	Northern pike eggs	safe level	as H_2S	NRCC 1977
0.026 ppm	96	Northern pike fry	LC_{50}	as H_2S	NRCC 1977
0.004 ppm	96	Northern pike fry	safe level	as H_2S	NRCC 1977
0.071 ppm	96	Walleye, eggs	LC_{50}	as H_2S	NRCC 1977
0.012 ppm	96	Walleye, eggs	safe level	as H_2S	NRCC 1977
0.007 ppm	96	Walleye, fry	LC_{50}	as H_2S	NRCC 1977
0.017 ppm	96	Walleye, juvenile	LC_{50}	as H_2S	NRCC 1977
0.0037 ppm	96	Walleye, juvenile	safe level	as H_2S	NRCC 1977
0.015 ppm	96	White sucker, eggs	safe level	as H_2S	NRCC 1977
0.0018 ppm	96	White sucker, fry	LC_{50}	as H_2S	NRCC 1977
0.0185 ppm	96	White sucker, juvenile	LC_{50}	as H_2S	NRCC 1977
0.002 ppm	96	White sucker, juvenile	safe level	as H_2S	NRCC 1977
0.032 ppm	96	Fathead minnows, juvenile	LC_{50}	as H_2S @ 20°C	NRCC 1977
0.003 ppm	96	Fathead minnows, juvenile	safe level	as H_2S	NRCC 1977

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	References
0.032 ppm	96	Fathead minnows, adult	LC_{50}	as H_2S	NRCC 1977
0.003 ppm	96	Fathead minnows, adult	safe level	as H_2S	NRCC 1977
0.032 ppm	96	Bluegill, juvenile	LC_{50}	as H_2S	NRCC 1977
0.002 ppm	96	Bluegill, juvenile	safe level	as H_2S	NRCC 1977
0.032 ppm	96	Bluegill, adult	LC_{50}	as H_2S	NRCC 1977
0.002 ppm	96	Bluegill, adult	safe level	as H_2S	NRCC 1977
0.042 ppm	10 day	*Gammarus pseudolomnacus*	LC_{50}	as H_2S	NRCC 1977
0.350 ppm	96	*Heragenia limbata*	LC_{50}	as H_2S	NRCC 1977
0.032	96	Bluegill	TL_m		WQC 1972
0.017	96	Juvenile walleye	TL_m		WQC 1972
0.032	96	Northern pike eggs	TL_m	continuous O_2 flow, 6 ppm	Becker 1973
0.009	96	Northern pike fry	TL_m	continuous O_2 flow, 2 ppm	Becker 1973
1,000	0.75 to 1	Goldfish	survival time	hard	Wilber 1969
100	3 to 4	Goldfish	survival time	hard	Wilber 1969
0.007	96	Walleye fry	TL_{50}	15°C, 6 ppm O_2	Smith 1972
1.38	48	Fathead minnow	TL_m		WQC 1963
Microorganisms					
1	not stated	Daphnia	lethal		WQC 1963
10 ppm	not stated	Daphnia	minimum lethal	dissolved Na_2S	NRCC 1977

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	References
Invertebrates					
0.84	96	Scud	TL_m		Verschueren 1977
0.316	96	Mayfly	TL_m		Verschueren 1977
0.02 to 0.3	96	Mayfly	LC_{50}	flow-through bioassay	Oseid 1974
0.111	96	Hog louse	LC_{50}	flow-through bioassay	Oseid 1974
1.07	96	Amphipod	LC_{50}	flow-through bioassay	Oseid 1974

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	References
Fish Kill Data					
0.05 to 1 (inorganic sulphides)	not stated	Trout	fatal	neutral and alkaline solutions	WQC 1972
1	not stated	Sea-run trout	toxic		WQC 1972
1	72	Pacific salmon	death		WQC 1972
Fish Toxicity Tests					
3	not stated	Pacific salmon	survival without injury		WQC 1972
3	not stated	Sea-run trout	survival without injury		WQC 1972

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	References
Invertebrates					
not stated	not stated	Oysters and other benthic organisms	lethal	H_2S generated from bottom sediments	WQC 1972
saturated	0.5	Bullia	lethal	H_2S bubbled	OHM-TADS 1981

6.3 Toxicity to Other Biota

6.3.1 Livestock.

Conc. (ppm)	Time (hours)	Species	Route	Result	Reference
800	5 min	Mammals	inhalation	LC_{LO}	RTECS 1979

6.3.2 Insects.

Conc. (mg/m^3)	Time (hours)	Species	Route	Result	Reference
380	16	Flies	inhalation	LC_{50}	Verschueren 1977
1,500	7 min	Flies	inhalation	LC_{50}	Verschueren 1977

6.3.3 **Plants.** Hydrogen sulphide does not generally constitute a problem to higher plants in the concentrations normally resulting from industrial-urban activities. The picture for important smaller organisms is less clear. Data reportedly suggest that under some conditions gaseous hydrogen sulphide may serve as the sole source of sulphur in the nutrition of a variety of agricultural crops. Hydrogen sulphide is largely present in the atmosphere in concentrations of 3 to 30 $\mu g/m^3$ and is derived from natural sources. The problems arise when man upsets this natural balance by creating a spill situation or as a result of a blowout at a gas well. Hydrogen sulphide appears to be unique among pollutants in that it injures the tips of fresh growth. Symptoms of chronic injury or growth effects are not known (NRCC 1977). Sax (1981) states that plants may be injured if exposed to greater than 5 ppm (7 mg/m^3) in air over 24 hours. The following table summarizes some of the available data:

Conc. (mg/m^3)	Species	Result	Reference
>0.3 ppm	Beans	toxic	Bennett 1980
1.38	Clover	toxic	Krause 1979
2.5	Spinach, garden pea	necrosis of leaves	Steubing 1979
30 ppb	Lettuce; sugar beet leaves	increases growth	Thompson 1979
<60	Buckwheat, clover, radish, soybean	sensitive; symptoms of injury	NRCC 1977
>600	Apple, cherry, grass, strawberry	resistant	NRCC 1977

6.4 Effect Studies

As stated earlier, the toxicity of sulphides is primarily due to the hydrogen sulphide molecule rather than the hydrosulphide (HS^-) or sulphide ($S^=$) ions. In aqueous solution, hydrogen sulphide acts as a very weak acid. At a 0.1 M concentration (3.408 g in 1 L of solution), the pH is 4.1, which equates to about 99.9 percent undissociated H_2S. The dissociation constant (K) is 10^{-7} for a 0.1 M solution at 1 atmosphere. As the pH of the solution is increased, the dissociation of the molecule to the hydrosulphide ion increases. It is apparent then, that the toxicity of aqueous hydrogen sulphide is dependent on pH and may account for the diversity in toxicity test results (WQC 1972; Cotton 1972). At pH 5 it is present in water as about 99 percent H_2S, while at pH 7 and pH 9 it is present as about 50 and 90 percent HS^-, respectively (NRCC 1977).

6.5 Degradation

6.5.1 Chemical Degradation. Hydrogen sulphide will dissipate by volatilization from neutral or acidic waters; after long periods in water, it may convert to elemental sulphur. Also, if heavy metals are present in solution, it may form insoluble salts over a period of time (OHM-TADS 1981).

6.5.2 Biodegradation. Sludge digestion is inhibited at 70 to 200 mg/L (Sax 1979).

6.6 Long-term Fate and Effects

Hydrogen sulphide does not have a bioaccumulation or food chain concentration potential (OHM-TADS 1981).

6.6.1 Studies. The residence time for hydrogen sulphide in the troposphere has been computed to be 1.4 to 1.7 days, on the basis of the global cycle estimates of sulphur compounds (NRCC 1977).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects of test animal and human exposures to hydrogen sulphide.

The toxicity of a material is due to its ability to damage or interfere with the metabolism of living tissue. Acute toxicity is defined as causing damage as the result of a single or short-duration exposure. Hydrogen sulphide is an acute poison (NRC 1981) and acts as an enzyme inhibitor (Meyer 1977). At concentrations in the range 500 to 1000 ppm, it acts primarily as a systemic poison, causing unconsciousness and death through respiratory paralysis. At concentrations below 500 ppm, it acts as an eye and respiratory irritant. The irritation action result from the reaction of the hydrogen sulphide with the alkali present in most surface tissue to form a sulphide salt which would be caustic (Sax 1979).

This chemical has been reported in the EPA TSCA Inventory. Published work on hydrogen sulphide toxicity was reviewed in 1977 (USDHEW 1977).

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for non-human mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for hydrogen sulphide are based upon its irritant properties and upon its action as a systemic poison. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
TLV® (8 h)	USA-ACGIH	10 ppm (14 mg/m^3)	TLV 1983
Acceptable ceiling	USA-OSHA	20 ppm (30 mg/m^3)	NIOSH/OSHA 1981
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	15 ppm (21 mg/m^3)	TLV 1983
Maximum allowable peak (10 min, once)	USA-OSHA	50 ppm (if no other measurable exposure occurs)	NIOSH/OSHA 1981

Guideline (Time)	Origin	Recommended Level	Reference
Ceiling concentrations (air)	USA-OSHA	20 ppm	Sax 1979
Ceiling concentration (10 min sampling, 10 h work shift)	USA-NIOSH	15 mg/m^3 (10 ppm)	NIOSH 1977
Ceiling (10 min)	USA-NIOSH	10 ppm	Doc. TLV 1981
15 minute average contamination limit	Saskatchewan	20 ppm (27 mg/m^3)	Sask. 1981
Other Human Toxicities			
IDLH	USA-NIOSH	300 ppm	NIOSH Guide 1978
LC_{LO} (30 min) (inhalation)	-	600 ppm	GE 1979; RTECS 1979
Evacuation required at this level	USA-NIOSH	70 mg/m^3	NIOSH 1977
Warning alert recommended	-	15-70 mg/m^3 (10-50 ppm)	Kirk-Othmer 1983
Long-term presence limit	Alberta	0.004 mg/m^3 (0.003 ppm)	Kirk-Othmer 1983

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour pressure, in mm Hg/TLV®, in ppm)

ITI = 1315.12 x (14 060 mm Hg (20°C)/10 ppm)

At 20°C, ITI = 1.8×10^6

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Liquid	Causes cold burns	GE 1979
Pure (gas) (10 to 20 min)	Localized warm sensation, erythema, and pigmentation similar to sunburn	Lang and Draize 1972. IN NIOSH 1977
Unspecified	Skin burns	ITII 1981
Unspecified	Skin penetration and toxicosis in people exposed to high concentrations over a long period of time	TDB (on-line) 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
>50 ppm (1 h)	Acute conjunctivitis with pain, lacrimation, and photophobia; in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium	NIOSH/OSHA 1981
>15 ppm (>8 h)	Painful conjunctivitis, sometimes with corneal erosion and spasm of the eyelids	Nesswetha 1969. IN NIOSH 1977
Unspecified	Keratitis and corneal blistering, pitting and opacity	NIOSH 1977
Unspecified	Palpebral edema, bulbar conjunctivitis, keratoconjunctivitis, and occular lesions	USDHEW 1977
Liquid	Corrosive to eyes	GE 1979

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Offensive odour suggesting rotten eggs (Doc. TLV 1981).

Odour Index: 17 000 000 (20°C) (Verschueren 1977).

Parameter	Media	Concentration	Reference
Odour Threshold (upper-lower)	In air	0.001-0.00001 ppm	OHM-TADS 1981
Odour Threshold	In air	0.18 ppm	ASTM 1980
Odour Threshold	In air	0.00018 mg/L (gas)	ASTM 1980
Recognition Threshold	In air	0.0047 ppm	ASTM 1980
Odour Threshold	In air	0.0047 ppm	CHRIS 1978
Odour Threshold	In air	>0.03 ppm	GE 1979
Odour Threshold	In air	0.02 to 0.003 ppm	NTIS PB 227486 1964. IN NIOSH 1977
50% Recognition Threshold	In air	1 ppm	Verschueren 1977
100% Recognition Threshold	In air	4.1 ppm	Verschueren 1977

Note: Although the foul odour of hydrogen sulphide is readily detectable in low concentrations, it becomes unreliable as a warning of dangerous concentrations of gas since continuous inhalation leads rapidly to olfactory fatigue (Matheson 1980).

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Taste Threshold (lower)	In water	0.05 ppm	ASTM 1980

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
12 000 ppm (No duration given)	Death (1 person exposed)	Simson 1971. IN NIOSH 1977
4000 to 2000 ppm (<20 min)	Death (1 person exposed)	Breysse 1961. IN NIOSH 1977
1400 mg/m^3 (<1 min)	Death of 1 out of 10, unconsciousness, abnormal ECG	Prouza 1970. IN NIOSH 1977
>2000 ppm	Systemic effects predominate over local irritant effects. Paralysis of respiratory centre, immediate death	CSC 1980
2000 to 1000 ppm (<20 min)	Hospitalization of 320 (out of 342 exposed), death of 22 including 13 in hospital, residual nervous damage in 4	McCabe and Clayton 1952. IN NIOSH 1977
2000 to 1000 ppm	Life threatening systemic effects predominate over local irritant effects. Immediate systemic symptoms. Stimulation of respiration (hypernea), followed by respiratory inactivity (apnea), collapse, asphyxia, and death within 30 min	CSC 1980
2000 to 1000 ppm	May cause coma after a single breath and be rapidly fatal. Convulsions may also occur	NIOSH/OSHA 1981
1000 ppm	Immediate unconsciousness, may be followed by coma, respiratory failure, and rapid death	Sax 1979
1000 ppm (<25 min)	Unconsciousness, low blood pressure, pulmonary edema, convulsions, and hematuria	Kemper 1966. IN NIOSH 1977
1000 ppm (instant)	Unconsciousness, death (5 people exposed)	Gas hazards in underground tanks and wells 1966. IN NIOSH 1977
1000 to 300 ppm (30 min)	May be fatal	Sax 1979

Exposure Level (and Duration)	Effects	Reference
1000 to 700 ppm	Life threatening. Systemic effects predominate over local irritant effects. Systemic symptoms within 30 min. Collapse, asphyxia and death within 1 h	CSC 1980
700 to 500 ppm	Life threatening. Systemic symptoms within 1 h. Headache, dizziness, unconsciousness, and death within 4 to 8 h. Serious irritation to respiratory tract and eyes (conjunctiva and epithelium) within 30 min. Coughing, bronchitis, pharyngitis, dyspnea, possible pulmonary edema, photophobia, conjunctivitis, and keratitis	CSC 1980
600 ppm	Fatal in 30 min	Sax 1979
<500 ppm (30 min)	Headache, dizziness, excitement, diarrhea, dysuria	Sax 1979
538 to 283 ppm	Unconsciousness (4 people exposed)	NIOSH 1977
500 to 300 ppm	Dangerous. Loss of sense of smell in ± 30 min. Severe eye irritation. Severe lung irritation with pulmonary edema after 30 min exposure	CSC 1980
<500 ppm	Immediate loss of consciousness	TDB (on-line) 1981
300 to 150 ppm	Severe irritation of eyes and lung. Loss of sense of smell in ± 30 min	CSC 1980
Several hundred ppm (>15 min)	Respiratory difficulty, pulmonary edema with hemorrhage, respiratory depression, neural damage (central or peripheral), and abnormalities in the cardiovascular system	Simson and Simpson 1971. IN NIOSH 1977
230 ppm (20 min)	Unconscious, arm cramps, low blood pressure (1 person exposed)	Ahlborg 1951. IN NIOSH 1977

Exposure Level (and Duration)	Effects	Reference
215 ppm	"Near fatal" poisoning of 2 pilots during the filling of water reservoirs of a fire fighting aircraft	TDB (on-line) 1981
150 to 50 ppm	Irritation. Olfactory paralysis can occur at 150 ppm	CSC 1980
50 ppm	May cause toxic symptoms	TDB (on-line) 1981
50 to 20 ppm	Minimal eye and lung irritation. Digestive upset possible	CSC 1980
25 to 14 ppm	78 subjects, burning eyes in 25, loss of appetite in 31, weight loss in 20, dizziness in more than 19, headaches in 32	Legg 1967. IN NIOSH 1977
20-15 mg/m^3 (4-7 h) (14-10 ppm)	Conjunctivitis, 6500 people exposed	Kirk-Othmer 1983
10 ppm	No effects	CSC 1980
8 to 0.002 ppm (intermittent pollution episodes over 2-month period)	Population of Terre-Haute; numerous complaints of nausea (13), headache, shortness of breath (4), sleep disturbance (5), throat and eye irritation (5)	NTIS PB227486 1964. IN NIOSH 1977
0.1 ppm	Irritation and sensory loss	TDB (on-line) 1981
SPECIES: Rat		
713 ppm (1 h)	LC_{50}	TDB (on-line) 1981
444 ppm (no time stated)	LC_{50}	RTECS 1979
SPECIES: Mouse		
673 ppm (1 h)	LC_{50}	TDB (on-line) 1981
SPECIES: Guinea pig		
1 mg/m^3 (8 h)	LC_{LO}	RTECS 1979
SPECIES: Mammal		
800 ppm (5 min)	LC_{LO}	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Human		
Concentration not specified	Higher incidence of cholecystitis, cholelithiasis, and cholangitis in 2,465 high-sulphur petroleum refinery workers	Bulatova et al. 1968. IN NIOSH 1977
Concentration not specified (subacute)	Signs and symptoms indicative of brain damage including: rigidity, abnormal reflexes, dizziness, sleep disturbance, and loss of appetite	Poda 1966 and Ahlborg 1951. IN NIOSH 1977
Unspecified concentration	No evidence to suggest that sulphide poisoning results in an impairment of oxygen transport by the blood. Some victims of hydrogen sulphide poisoning exhibit frank cyanosis, suggesting that respiratory tract obstruction is more common in this condition than is generally accepted	TDB (on-line) 1981
Unspecified concentration	Interference with cellular respiration through poisoning of the cytochrome system	McCormack 1975. IN NIOSH 1977
Sublethal concentration not specified	After sublethal exposure, recovery is slow. Victims have a residual cough, cardiac dilation, slow pulse, peripheral neuritis, albuminuria, amnesia or psychic disturbances	TDB (on-line) 1981
Unspecified concentration	Repeated exposure results in increased susceptibility, so that eye irritation, cough, and systemic effects may occur at concentrations previously tolerated without effects	NIOSH/OSHA 1981

7.4.2 Ingestion. Hydrogen sulphide is a gas at normal atmospheric pressure and temperature and thus ingestion is unlikely. Contact with the liquid (b.p. = -60.7°C) would cause frostbite burns. The ingestion of small amounts of "aqueous" hdyrogen sulphide into the stomach is not considered hazardous (Meyer 1977).

7.4.3 Carcinogenicity, Mutagenicity and Teratogenicity. No reports associating hydrogen sulphide in air with carcinogenesis, mutagenesis, or teratogenesis were found in the literature (NIOSH 1977).

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of nose, throat and eyes.
2. Olfactory fatigue (ITII 1981).
3. Headache.
4. Rhinitis.
5. Dizziness, vertigo (TDB (on-line) 1981).
6. Giddiness, euphoria and confusion.
7. Muscular weakness.
8. Cold sweat (TDB (on-line) 1981).
9. Muscle cramps.
10. Pharyngitis, bronchitis (ITII 1981).
11. Breathing difficulties.
12. Hyperpnea (CHRIS 1978).
13. Urogenital system albuminuria (TDB (on-line) 1981).
14. Palpitations, tachycardia, arrhythmia and slow pulse (TDB (on-line) 1981)
15. Cyanosis (TDB (on-line) 1981).
16. Peripheral neuritis (TDB (on-line) 1981).
17. Pneumonia (ITII 1981).
18. Convulsions (NIOSH/OSHA 1981).
19. Pulmonary edema (GE 1979).
20. Coma.
21. Respiratory paralysis (CHRIS 1978).
22. Death.

7.5.2 Ingestion. As noted previously, ingestion is unlikely and has not been reported.

7.5.3 Skin Contact.

1. Local irritation of the skin and minor burns (CSC 1980).
2. Localized warm sensation, erythema and pigmentation similar to a sunburn (NIOSH 1977).
3. Contact with liquid will cause severe burns.

7.5.4 Eye Contact.

1. Eye contact with liquid and gas will cause painful burns and irritation (MCA 1968).
2. Lacrimation.
3. Photophobia (TDB (on-line) 1981).
4. Inflammation of conjunctiva.
5. Palpebral edema, bulbar conjunctivitis (USDHEW 1977).
6. Keratoconjunctivitis, vesiculation of corneal epithelium (NIOSH 1977).
7. Risk of serious lesions.
8. Corneal opacity (TDB (on-line) 1981).

7.6 Human Toxicity to Decay or Combustion Products

Hydrogen sulphide produces sulphur dioxide when burned in air (Partington 1958). Sulphur dioxide is a colourless, nonflammable gas with a strong suffocating odour. It is extremely irritating to the eyes and respiratory tract (Merck 1976). The irritation of the mucous membranes probably results from the action of sulphurous acid formed where the highly soluble gas dissolves. Short-term exposure causes bronchoconstriction. The magnitude of the response is dose-related. The TLV® for sulphur dioxide is 2 ppm (8 h-TWA) and 5 ppm (STEL) (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Hydrogen Sulphide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Heat		x					x						Emits sulphur oxides when burned	Sax 1979
Fire		x	x										Moderate explosion hazard	Sax 1979
SPECIFIC CHEMICALS														
Acetaldehyde											x			NFPA 1978
Bromine Pentafluoride		x	x											NFPA 1978
p-Bromobenzenediazonium Chloride			x								x			Bretherick 1979
Chlorine Monoxide		x												NFPA 1978
Chlorine Trifluoride			x											NFPA 1978
Chromic Anhydride						x							Decomposition when heated	NFPA 1978
Copper	x												Powder may heat to redness on exposure to air/H_2S mixture	NFPA 1978

8.1 Compatibility of Hydrogen Sulphide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Fluorine		x											Ignites on contact	NFPA 1978
Lead Dioxide	x	x											Almost instantly on contact	NFPA 1978
Nitric Acid	x												Incandesces with fuming nitric acid	NFPA 1978
Nitrogen Iodide						x								NFPA 1978
Nitrogen Trichloride			x			x					x		Upon contact	Bretherick 1979
Nitrogen Trifluoride			x										Explosion occurs upon ignition of the mixture	NFPA 1978
Oxygen Difluoride			x										Upon mixing	NFPA 1978
Phenyl Diazonium Chloride			x										Upon mixing	NFPA 1978
Rust		x											May ignite if passed through rusty iron pipe	Bretherick 1979
Silver Fulminate			x								x			Bretherick 1979

8.1 Compatibility of Hydrogen Sulphide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Soda Lime	x	x											Incandesence in air, may react with sufficient heat to ignite surrounding combustibles	Bretherick 1979
Sodium											x		Upon contact with moist H_2S	NFPA 1978
Sodium Peroxide		x									x			NFPA 1978
CHEMICAL GROUPS														
Epoxides	x				x									EPA 600/2-80-076
Polymerizable Compounds	x				x									EPA 600/2-80-076
Metal Oxides		x	x											Bretherick 1979
Oxidizing Agents	x	x	x								x			Bretherick 1979

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 **Fire Concerns.** Hydrogen sulphide is a flammable gas which produces sulphur dioxide gas when burning. It forms explosive mixtures with air and may travel along surfaces to ignition sources and flash back (GE 1979; NFPA 1978). It can be dangerously reactive with oxidizing agents as well as other materials. Containers of hydrogen sulphide may explode if exposed to fire (EAG 1978).

9.1.2 **Fire Extinguishing Agents.** Use water spray to cool containers involved in a fire to prevent rupture. Apply water from a safe distance.

Small fires:	Dry chemical or CO_2.
Large fires:	Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay clear of tank ends (ERG 1980; EAG 1978).

9.1.3 **Evacuation.** The following information consists of evacuation distances which appear in the literature. Important parameters such as spill quantity, concentration level to which evacuation is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zones in Section 5.3 of this manual. The following are evacuation distances from the immediate danger area of a spill, based on prevailing winds of 10 to 19 km/h (EAG 1978).

Approximate Size of Spill	Distance to Evacuate From Immediate Danger Area	For Maximum Safety, Downwind Evacuation Area Should Be
20 m^2	75 m (96 paces)	645 m long, 320 m wide
35 m^2	100 m (132 paces)	1125 m long, 480 m wide
55 m^2	130 m (196 paces)	1290 m long, 645 m wide
75 m^2	150 m (192 paces)	1610 m long, 805 m wide

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (GE 1979). Use water spray to protect men effecting the shut-off (NFPA 1978). If a container is leaking, remove the container outdoors and rotate it so gas instead of liquid is leaking (OSHA MSDS 1979). Hydrogen sulphide gas leaking from a container can be passed through a ferric chloride ($FeCl_3$) solution with a trap in line to prevent siphoning back (Sherritt MSDS 1981). It is well known that hydrogen sulphide is a mild reducing agent and can reduce ferric ions to ferrous ions by the reaction:

$$2Fe^{+3} + H_2S\,(g) \rightarrow 2Fe^{++} + S_{(s)} + 2H^{+}$$

The reaction will thus produce colloidal sulphur.

The leaking gas may also be absorbed directly into solutions of sodium carbonate or hydroxide (Na_2CO_3, NaOH). The weakly acidic dissolved gas will be converted to the soluble sulphide salt of sodium in the basic solutions (MCA 1968). It is advisable to keep the volume of solution as small as possible since the resulting sodium sulphide solution must be further treated for disposal. Although other methods for absorbing hydrogen sulphide are recommended in the literature, the ones included above are thought to be the most simple for emergency situations.

9.1.4.2 Spills on land. When spilled in liquid form, contain if possible by forming mechanical and/or chemical barriers to prevent spreading (EPA 670/2-75-042). Sorbents such as activated carbon are recommended for containment and to reduce vapours (CG-D-38-76). Rapid boiling and evaporation will occur. Vapours can be "knocked down" with water spray if necessary, but the resulting contaminated water must be contained and subsequently treated for disposal.

9.1.4.3 **Spills in water.** Contain contaminated water if possible. Elemental sulphur may be precipitated by compressor aeration or oxygenation. Sorbents such as activated carbon and anion exchange resins are recommended as media for solubilized hydrogen sulphide (PPP 1982; OHM-TADS 1981). If the above equipment or materials are not available, the weakly acidic water can be neutralized with agents such as lime (CaO), sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3) (EPA 670/2-75-042; MCA 1968). The resulting solution, however, must be further treated to remove the sulphide ion.

9.1.5 Cleanup and Treatment.

9.1.5.1 **General.** The recommended treatment for contaminated water is the same as described in Section 9.1.4.1.

9.1.6 **Disposal.** Waste solutions of hydrogen sulphide must never be discharged directly into sewers or surface waters. The contaminated material must be treated such that the dissolved gas is removed or converted to a more easily handled form of sulphur and then removed.

Following this treatment at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill and the water returned to the environment. Typical waste recovery technologies that lend themselves to the removal of hydrogen sulphide or sulphide salts from waste water are carbon adsorption, reverse osmosis, evaporation, and ion exchange (PPP 1982).

9.1.7 **Protective Measures.** For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be hydrogen sulphide:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid hydrogen sulphide or from contact with vessels containing liquid hydrogen sulphide (NIOSH/OSHA 1981).
- Splash-proof or chemical safety goggles are also recommended for eye protection (NIOSH/OSHA 1981; MCA 1968).

- Cloropel has been recommended as a chemical suit material (excellent resistance) for protection against hydrogen sulphide (EE-20).
- Any clothing which becomes wet with liquid hydrogen sulphide should be removed immediately and not reworn until the hydrogen sulphide has evaporated (NIOSH/OSHA 1981).
- Eye wash stations and safety showers should be readily available in areas of use and spill situations (GE 1979).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where hydrogen sulphide is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required above 10 ppm
Gas Concentration 30 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases or hydrogen sulphide. Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.8 Special Precautions for Storage and Use. Store in a cool, well-ventilated, fire-resistant area (outside or detached storage preferred) away from sources of heat and ignition. Keep cylinders away from oxidizing agent and out of direct sunlight. Ground lines and equipment used with H_2S to reduce possibility of static spark initiating fire or explosion (GE 1979). Protect cylinders against physical damage (NFPA 1978).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus the number of experiences is not an indication of the problems or frequency of spillage.

10.1 **Pipeline Leak** (PC SRNMP 1982; HMIR 1980)

A leak of hydrogen sulphide vapour occurred in a pipeline connecting a 100 tonne storage tank, containing liquid hydrogen sulphide, to a deuterium production facility. Approximately 150 employees were evacuated from the immediate vicinity of the leak. Major modes of transportation (land, air, water) were either closed or rerouted to prevent any danger of contact with the escaping gas. Response personnel, equipped with self-contained breathing apparatus and plastic suits, found that hydrogen sulphide was escaping through a cracked weld in the pipeline. It was noted that the crack expanded to about 5 cm in length before it sealed with "hydrate" 8 hours later. It is assumed that the crack was sealed with water ice resulting from the cooling associated with the hydrogen sulphide expanding through the crack.

During release of hydrogen sulphide gas from the pipe, plant personnel monitored the air around the dyke surrounding the affected storage tank and found that H_2S concentrations were ranging from 10 ppm to 100 ppm, before the crack self-sealed. Response personnel found that the only way to remove the contents of the tank without producing any vibration to open the sealed crack was to use a compressor and remove hydrogen sulphide gas from the vapour space of the tank. The compressor was positioned at the top of the tank. The hydrogen sulphide vapour removed from the affected tank was then recompressed and fed through pipelines to other storage tanks on-site. Steam lances were used to vaporize the liquid hydrogen sulphide in the tank to facilitate removal. It took a period of 9 days to complete the transfer of 80 tonnes of liquid hydrogen sulphide from the affected tank into other storage tanks.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Hydrogen Sulphide in Air

11.1.1 Spectrophotometric (NIOSH 1977). A range of 8.5 to 63 mg/m^3 (6.10 to 45.20 ppm) of hydrogen sulphide in air may be determined spectrophotometrically.

A known volume of air is drawn through a 25 mL midget impinger containing 10 mL of an absorbing solution. A sample volume of 2 L is recommended at a flow rate of 200 mL/min. The absorbing solution is made in two stages. The cadmium sulphate-STRactan® solution is made by dissolving 8.6 g of cadmium sulphate-octahydrate in approximately 600 mL of water and adding 20 g of STRactan 10® and diluting to 1 L. The cadmium hydroxide-STRactan® absorbing solution is prepared by pipetting 5 mL of sodium hydroxide solution (0.6 g sodium hydroxide/L) and 5 mL of cadmium sulphate-STRactan® solution into a 25 mL midget impinger.

The absorbing solution and the deposit in the impinger bottom are quantitatively transferred to a 250 mL volumetric flask. A 50 mL volume of distilled water is used to rinse the impinger. The impinger stem is rinsed outside and inside with 20 mL each of distilled water. All rinsings (90 mL total) are added to the volumetric flask. The amine test solution is prepared by diluting a 25 mL aliquot of amine-sulphuric acid stock solution to 1 L with diluted (1:1, v/v with water) sulphuric acid. The stock solution is a mixture of 12 g para-aminodimethylaniline dissolved in 50 mL concentrated sulphuric acid and 30 mL water. A 0.5 mL volume of ferric chloride solution (100 g ferric chloride hexahydrate/100 mL) is added to the flask and the mixture brought to volume with distilled water. The mixture is allowed to stand for 20 min.

The absorbance is determined using a suitable spectrophotometer or colourimeter at 670 nm using a reagent blank as a reference.

11.2 Qualitative Method for the Detection of Hydrogen Sulphide in Air. Hydrogen sulphide may be determined in air by use of a Drager tube for hydrogen sulphide. Air is drawn through the detector tube by use of a Drager pump. A colour change on the indicating layer from colourless to pale brown indicates the presence of hydrogen sulphide. This method may also be used for a quantitative determination, depending on the number of pump strokes (Drager 1979).

11.3 Quantitative Method for the Detection of Hydrogen Sulphide in Water

11.3.1 Spectrophotometric (AWWA 1976). A range of 0 to 20 ppm of sulphide may be determined using the methylene-blue method of colour development and spectrophotometric determination. A minimum of 1 L of representative sample is collected in an appropriate container. A 7.5 mL volume of sample is placed in each of two matched test tubes. An amine-sulphuric acid reagent stock solution is prepared by dissolving 27 g of N,N-dimethyl-p-phenylene diamine oxalate in a cold mixture of 50 mL concentrated sulphuric acid and 20 mL of distilled water. The diluted stock solution is a 25 mL dilution in 975 mL of 50 percent sulphuric acid. The stock solution and diluted stock solution should be stored in amber glass bottles. A 0.5 mL volume of the diluted reagent is added to one of the two matched test tubes, labelled tube A. The mixture is cooled and diluted to 100 mL. Ferric chloride solution is made by dissolving 100 g of ferric chloride hexahydrate in 40 mL of water. A 0.15 mL volume of this solution is added to test tube A and mixed. To test tube B, add 0.5 mL of 50 percent sulphuric acid solution (400 g/800 mL distilled water) and 0.15 mL ferric chloride solution and mix. The colour is allowed to develop for 10 min. Methylene-blue solution is prepared by dissolving 1.0 g of USP grade dye in 1 L of water. It is added to test tube B until the colour matches that in test tube A. For the spectrophotometric determination, a portion of test tube B is used to zero a suitable spectrophotometer using 1 cm cells at a wavelength of 664 nm. The sulphide is determined using a calibration curve.

11.4 Qualitative Method for the Detection of Hydrogen Sulphide in Water

The sample is collected as in Section 11.3.1. A 2 mL volume of sample is placed in a test tube and basified by adding 6 M ammonium hydroxide, then adding 2 mL in excess. The solution is then centrifuged and the supernatant discarded. A 2 mL volume of water is added to the precipitate. The mixture is again centrifuged and the washings are discarded. A 2 mL volume of 6 M hydrochloric acid is added to the precipitate and a piece of lead acetate-moistened filter paper is held over the mouth of the test tube. A brown or black stain indicates a sulphide (Welcher 1955).

11.5 Quantitative Method for the Detection of Hydrogen Sulphide in Soil

11.5.1 Titrimetric (Hesse 1972). Total sulphur may be determined by reduction as hydrogen sulphide in soil.

A 1 g sample of 0.15 mm soil is ground in an agate mortar with 5 g of reduced iron powder. The 0.15 mm soil is prepared by grinding the contaminated "as received" soil and screening it through a 0.15 mm sieve. One half of the mixture is placed in a combustion tube made of fused silica, along with an additional 2 g of reduced iron on top of the mixture. The tube is placed in a heating block containing a top and bottom heating coil. The mixture and top layer of iron are placed such that both are below the top coil. The tube is best suspended by a stiff wire support so its position can be varied. The top heating coil is switched on for 10 min, then the bottom coil, and the heating continued for an additional 10 min. After the coils have been turned off, the heating block is allowed to cool. The combustion tube is placed horizontally in the reaction flask of the apparatus for liberating absorbed hydrogen sulphide; nitrogen gas is passed through immediately. A 25 mL volume of 0.02 M potassium hypochlorite solution and 25 mL of water are placed in the absorbing flask connected to the air condenser of the apparatus. 50 mL of dilute (6 N) hydrochloric acid are then added to the reaction flask. When visible reaction has ceased, the mixture is heated for 45 min. Nitrogen is then passed through more rapidly for a few minutes and the absorption flask is removed. A 5 mL volume of 10 percent potassium iodide solution and 5 mL of 10 percent sulphuric acid solution are added to the flask. The liberated iodine is titrated with standardized 0.02 M sodium thiosulphate using starch as indicator. A blank determination should also be made.

11.6 Qualitative Method for the Detection of Hydrogen Sulphide in Soil

The sample is prepared as in Section 11.5 up to the rapid passing of nitrogen gas through the reaction flask.

A 2 mL volume of sample is placed in a test tube and basified by adding 6 M ammonium hydroxide. Then a 2 mL excess is added. The solution is stirred and 2 mL of 0.5 M tetramine zinc nitrate solution are added. The solution is then centrifuged and the supernatant discarded. A 2 mL volume of water is added to the precipitate. It is centrifuged and the washings are discarded. A 2 mL volume of 6 M hydrochloric acid is added to the precipitate and a piece of lead acetate-moistened filter paper is held over the mouth of the test tube. A brown or black stain indicates a sulphide (Welcher 1955).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc.	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immision concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
T_d	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
T_s	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight